KINETIC STUDIES OF THE POLYMERIZATION OF ETHYLENE USING A NOVEL ZIEGLER CATALYST

DAVID GEORGE BOUCHER

A thesis submitted for the Degree of Master of Science in the Faculty of Science and Engineering.

Chemistry Department

October, 1973

SYNOPSIS

The applied objective of this research was to prepare an ultra-high molecular weight polyethylene with improved physical properties more suited for use in surgical implants, especially artificial hip-joints, than those of current materials. A recently discovered Ziegler catalyst system involving aluminium alkyls and titanium (III) chloride prepared using a Grignard reagent was used to obtain material of high molecular weight at very high levels of catalytic activity. Using this system, conditions have been established for preparing polymer of viscosity number 25 cm^3gm^{-1} x 10^{-2} ($\overline{M}_n \sim 1.4 \times 10^6$) and titanium content 1 ppm compared with viscosity number 17 cm^3gm^{-1} x 10^{-2} and titanium content 10 ppm for the commercial material Hostalen GUR. The processes required for the unusually stringent purification of reagents necessary to obtain the benefit of the exceptional activity of the present catalyst system (employed down to very low concentrations: 1 x 10^6 molar) are described.

A kinetic study of the reaction was undertaken in which the rate of polymerization has been observed in relation to the concentration of aluminium triethyl, concentration of titanium (III) chloride and the reaction temperature. The conditions in which mass transport limitations occur were defined, and a value for the maximum rate in the absence of such effects determined. The value of the overall apparent activation energy of the reaction was estimated as 75.8 $kJ.mole^{-1}$ (18 $kcal.mole^{-1}$).

The behaviour of the number average molecular weight of the polymer was studied as a function of catalyst concentration and temperature. Viscosity measurements were used to estimate $\bar{M}_n$, from which values of the concentration of active polymerization sites, propagation rate constant, transfer rate constant and the lifetime of the growing polymer chain were found both for the magnesium reduced system and for a conventional catalyst system. Results indicate the magnesium reduced system has about 130 times the active sites found in the conventional system but that the intrinsic catalytic activity of each site is not quite as high. The enhanced activity of the catalyst is attributed to the disorder present in the particles. This is thought to arise from the alkyl magnesium halide preparation method.

ACKNOWLEDGEMENTS

I wish to thank Chas. F. Thackray Limited for the provision of the grant to support this work. I am indebted to Mrs. L. A. Price for assistance with the preparative experiments at elevated pressure and the determination of viscosity measurements. I am also grateful to Professor R. N. Haward and Dr. I. W. Parsons for their valuable discussions and helpful advice. I should also like to thank Mrs. D. S. Seal for typing the manuscript.

C O N T E N T S

INTRODUCTION

Although polymer science is one of the youngest branches of chemistry, polymers are at least as old as man himself, for the most important substances in nature, cellulose, proteins, nucleic acids and enzymes are all polymeric compounds. However it is only in relatively recent times that scientific studies have been made of polymeric materials and from these the possibility of their syntheses by suitable chemical reactions developed.

The period of the 1939 - 1945 war stimulated intense activity in macromolecular chemistry although it had been a subject of scientific interest and technological advancement since the beginning of the nineteen thirties. Prior to this time with the exception of the discovery of "Bakelite" most developments in the commercial exploitation of polymers were confined to the processing of naturally occurring materials, such as wool, cotton, cellulose, and leather; synthetic polymers being virtually unused as commercial materials.

Polymers

Polymer is a word of Greek derivation meaning "many parts" (polus - many; meros - parts) and is used to describe substances whose molecules are made up of many similar units joined together. These single units are generally small groups of atoms but can be single atoms. The molecules from which a polymer is formed are known as monomer units. Two such monomer units chemically combined form a dimer, three a trimer, four a tetramer, etc.

The name "Polymer" is normally confined to cases when the molecular weight exceeds about 10,000 - usually about 200 - 500 units upwards. At this stage the material has properties which are fundamentally different from those of the original unit molecules, this is mainly due to the very great size of the macromolecules. Shorter chains with up to about 100 monomer units joined together are known as oligomers.

In macromolecular chemistry, unlike traditional organic chemistry where synthetic materials are indistinguisable from their natural counterparts, there are no simple syntheses from low molecular weight compounds of the natural high polymeric materials. Therefore as the characteristics of polymeric materials differ substantially from low molecular weight materials it is often most convenient to classify macromolecules by their source of origin as shown in Table I.

Early developments in synthetic polymers

Natural high polymers have been utilised by man for thousands of years. Most foods and many clothing materials e.g. wool, cotton, leather, silk, contain cellulose, starch and protein macromolecules. The industrial usage of synthetic polymeric materials, however, is quite recent. It is only during the last three decades that the development of industries for the production of synthetic fibres and filaments and preparation of synthetic resins and plastics has occurred.

The first industrial processes involved the conversion

of natural polymers. Most of the early commercial effort was centred on the production of artificial fibres and the fabrication of articles from rubber. In the early part of the 19th century rubberised fabrics were successfully produced and in 1839 Goodyear developed a technique for the vulcanisation of rubber. The "Regeneration of cellulose" was the earliest technique for the preparation of synthetic fibres; as early as 1855 an "artificial silk" had been made from nitrocellulose. However, it was not until 1883 that J. W. Swan produced cellulose filaments ("rayon") by a process which could be adapted for commercial exploitation.

Table I

Classification of macromolecular substances

I Naturally occurring substances.

a. Hydrocarbons	e.g. rubber, gutta percha
b. Polysaccharides	e.g. celluloses, starches
c. Polynucleotides	e.g. nucleic acids
d. Proteins and enzymes	
e. Lignins and tannins	

II Conversion products of natural substances

Vulcanised rubber

Rayon and cellophane

Cellulose nitrate

Leather

III Synthetic materials

a. Condensation polymers

Polyamides ("nylon")

Polyesters

Polyurethanes

Polycarbonates

Phenol-aldehyde resins ("Bakelite")

Amino resins

Epoxy resins

Polyethers

Silicones

b. Addition polymers

Polystyrene

Polyvinyl chloride

Polyvinyl acetate

Polyethylene ("polythene")

Polypropylene

Polytetrafluorethylene ("teflon")

Acrylic polymers ("perspex", "orlon")

The first polymer material used for moulding was probably "celluloid" originally discovered by Alexander Parkes in Birmingham in 1865. He prepared a horn-like material, which he called "Xylonite", from nitrocellulose, an alcohol and camphor. In 1870 J. W. and J. S. Hyatt patented in America a commercial process for the production of a material called "celluloid" from the same starting materials. The discovery of the polymerization

of casein with formaldehyde in 1897 created one of the early plastics.

It is probably the relatively extensive usage of "Bakelite" during the 1920's which marks the first milestone in synthetic polymer technology. Professor A. von Baeyer originally prepared the artificial resin from phenol and formaldehyde in 1872, but it was in 1908 that a process for its commercial use was developed by L. H. Baekeland. However, the early production of polymeric materials was entirely empirical and only more recently have intensive fundamental studies been undertaken. In fact it was not until 1920 that Staudinger first proposed the concept of polymers.

By the time of the 1939 -1945 war the value of synthetic polymers had been realised and commercial interest aroused to the development of these new materials which in several cases became intensified by the demands of the war effort. Many of the contemporary synthetic fibres were discovered about this time. In 1935 W. H. Carothers synthesised "nylon" from adipic acid and hexamethylene diamine. "Rayon" was produced from cellulose by the viscose process of C. F. Cross and E. J. Bevan. In 1946 J. R. Whinfield produced "terylene" ("dacron") by the combination of terephthalic acid and ethylene glycol.

Often new materials found great demand during the war period, in many cases as alternative replacements to ones which had become unobtainable. Reactions of butadiene and styrene discovered in the nineteen hundreds were developed

to produce a synthetic rubber. "Perspex," polymethylmethacrylate, was in demand for use as the glazing material in aeroplanes. Techniques such as injection moulding first introduced in the nineteen thirties with cellulose plastics were adapted to cope with new synthetic materials. During the late nineteen thirties and early forties new polymers, such as polystyrene, polyvinylchloride and polyethylene, appeared, the latter being almost entirely absorbed in production of the newly developed radar equipment.

The historical development of polyethylene

The first recorded instance of polyethylene is probably by Pechmann[1] in 1898 when he tentatively identified the recrystallized product of the reaction of diazomethane in ether as polymethylene. Further use was later made of this synthetic route by Buckley, Cross and Ray[2] who added a copper catalyst to prepare polymethylene, polyethylidene and polypropylidene, subsequently found to have molecular weights between 200 and 14,000. During the nineteen twenties polyethylene was prepared by several methods[3] but none attracted commercial interest because of the high cost involved.

In the early nineteen thirties the advance of high pressure reaction techniques made it possible to produce pressures of 3,000 atmospheres (304 MNm^{-2}), and in 1934 Fawcett and Gibson[4] reported successful polymerizations

of various monomers under high pressure. However, it was not until December 1935 when eight grammes of the polyethylene were produced in small scale apparatus that Imperial Chemical Industries Ltd. decided to proceed with the development of the material which resulted in a patent[5] on the process in 1937 and the construction of a continuous pilot plant. In 1942 the I.C.I. process went into full scale production and the following year manufacture under licence was started in America.

The next important milestone in the history of the material was the development of low pressure synthesis processes. The first of these, discovered by K. Ziegler[6] in 1954, uses a catalyst precipitated by the reaction of transition metal salts and metal alkyls. This was followed in 1955 by the discovery of another new low pressure process by the Phillips Petroleum Company[7] using preformed catalysts of transition metal oxides on supports of high surface area e.g. silica. One of the important findings resulting from the discovery of low pressure catalysts was that the polymer produced was essentially a linear chain material in comparison to that produced by the high pressure processes which was highly branched.

Another important result was the ability of such catalysts to regulate the stereochemistry of higher α-olefin polymers which enabled the synthesis of highly isotactic polypropylene. This polymer in contrast to its atactic counterpart is a useful and saleable material.

CHAPTER I

POLYETHYLENE : ITS PREPARATION AND PROPERTIES

The three basic methods of polyethylene synthesis previously mentioned are still the contemporary industrial techniques. These methods are the high pressure radical polymerization and the low pressure catalytic processes using either "Ziegler" or "Phillips" type catalysts. Characteristics of typical material from the three processes are shown in Table 2. The notable differences in the properties of materials from the three processes are principally due to changes in the linearity, molecular weight and molecular weight distribution of the polymer molecules. However, in all three processes the polymer is formed by addition polymerization; the monomer units being joined by reaction involving the carbon-carbon double bonds in the ethylene molecules.

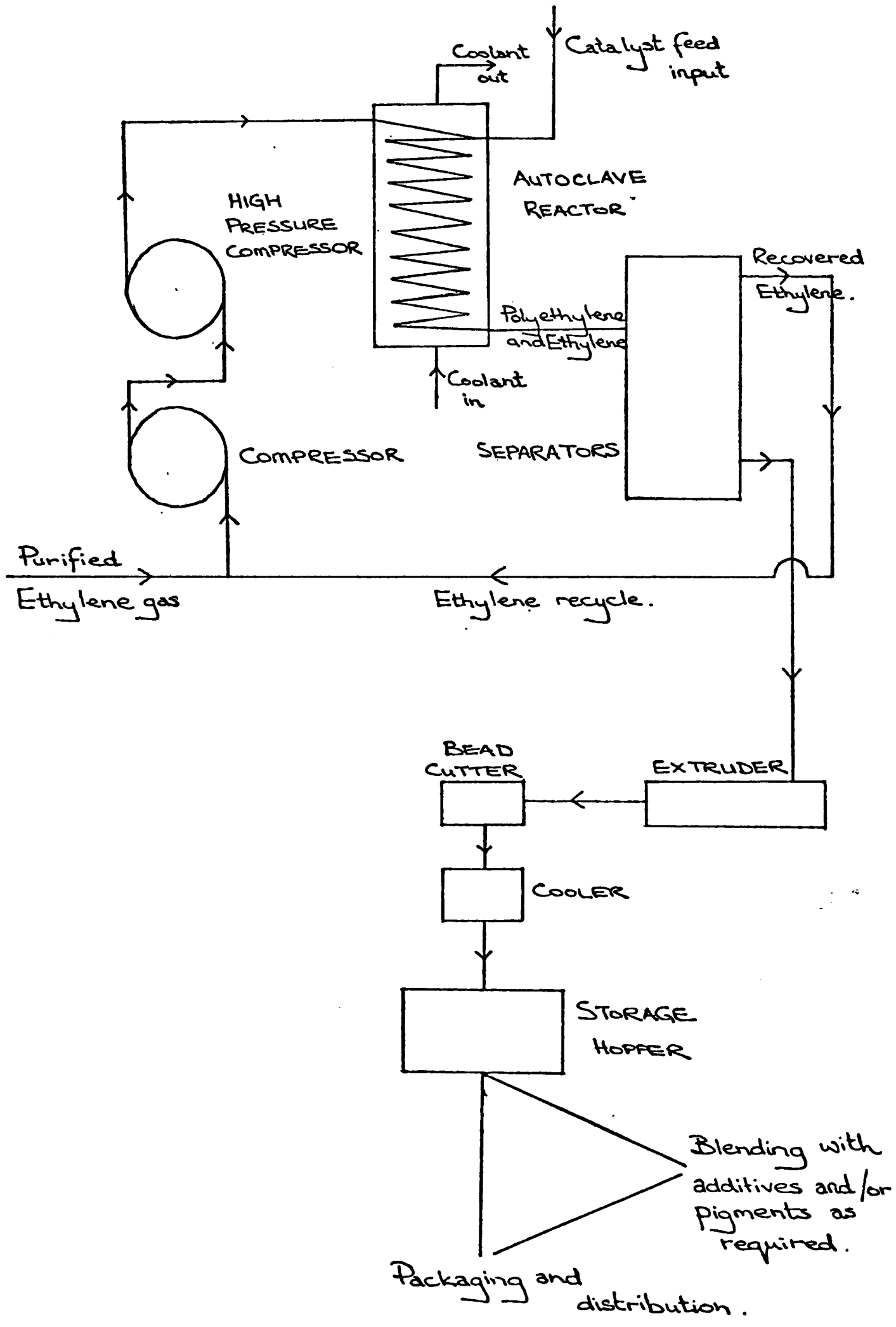
High pressure-low density polyethylene

There has been a dramatic increase in the consumption of polyethylene since the original 455 tons per annum I.C.I. plant was constructed. The current market is estimated at 2 million tons per annum[8] and the material finds extensive use for films, moulded goods, tubing and in electrical insulation applications. However, the synthetic process for low density polyethylene has not basically altered, the plant employed being shown schematically in Figure 1.

In the original I.C.I. process[5] high purity (99.8%) ethylene monomer is compressed to the polymerization

Continued on page 10 at end of Table 2.

Figure 1.



The high pressure method for polyethylene manufacture as used in the I.C.I. type processes.

Table 2

Characteristics of typical polyethylene made by three methods of industrial synthesis

Property	Polyethylene material		
	High pressure low density e.g. Union Carbide DYNH	Low pressure high density Ziegler type e.g. Super Dylan	Low pressure high density Phillips type e.g. Marlex 50
Density $gm.cm^{-3}$	0.92	0.95	0.96
% Crystallinity	65	85	95
Crystallite size, nm.	19	36	39
Melting point, $^{o}C.$	112	130	135
Tensile strength, MNm^{-2}	14	25	30
Elongation, %	500	100	30
Impact strength Izod test, ft.lb/in. notch	>16	4	3
Hardness, Shore D	50	65	70
Unsaturation (Double bonds per 1000c)	0.6	0.7	1.5
% Distribution:			
Vinyl $R\sim\sim CH=CH_2$	15	43	94
Trans $R\sim\sim CH=CH\sim\sim R^1$	17	25	5
Vinylidene $R\sim\sim C(R^1)=CH_2$	68	32	1

CONTD...

Property	Polyethylene material		
	High pressure low density e.g. Union Carbide DYNH	Low pressure high density Ziegler type e.g. Super Dylan	Low pressure high density Phillips type e.g. Marlex 50
Short chain branching: (groups per 1000C)	21.5	3	<1.5
Distribution: (gps/1000C)			
Terminal methyl	4.6	(~2)	(<1.5)
Branch methyl	(2.5)	-	-
Branch ethyl	14.4	1	<1

( ) - Values are assumed.

Most of the data is reproduced from work presented by R. V. Jones and P. J. Boeke, Ind. Eng. Chem., 48, 1155, (1956). D. C. Smith, Ind. Eng. Chem., 48, 1161, (1956).

---

pressure of 150 MNm^{-2} (1,500 Atmospheres) and passed into a reactor at a temperature of about 200°C. The radical polymerization is initiated by the addition of a controlled quantity of oxygen to the reactor. Reaction occurs to the extent of 15 – 25% conversion before the pressure of the reaction mixture is reduced in a series of separators. The unreacted ethylene is recovered from these and recycled whilst the molten polymer is finally extruded and made into beads which form the crude product. Further processing may blend in additives and pigments as necessary.

The reactor used must be constructed to efficiently deal with the relatively high heat of polymerization. Normally a continuous process is used and the plant consists either of a fine tubular system cooled by water circulation or a tower autoclave in which heat is dissipated by the addition of a liquid such as water to the monomer feedstock which may be dissolved in benzene or chlorobenzene. Batch polymerizations are unsuitable for the high pressure technique as good control requires uneconomically long reaction times and at high conversion chain branching becomes excessive, producing material of poor physical properties. Initiator and the other reagents may be added to the monomer at several stages throughout the reaction to maintain concentrations. Alternative initiators to oxygen have also been employed to extend the range of material produced. In many cases the use of specially active initiators and chain transfer agents can give lower operating temperatures which often combined with higher pressures result in a more linear product.

The macromolecules produced by high pressure process tend to have side chains because it is a radical reaction. The side chains are normally a few carbon atoms in length but can occur up to five times for each 100 carbon atoms of the main chain. The result is that high pressure processes produce a material of low crystallinity (50 - 60%) as the branches tend to hinder the formation of crystallites and spherulites. It is generally found that

the greater the linearity of the chains the higher the ratio of crystalline regions to amorphous ones, becomes. The density and many of the physical properties of the material have been shown to be closely related to the measured crystallinity.

Low pressure - high density polyethylene

The market for high density polyethylene has grown alongside that for the low density material since the discovery of the low pressure processes in the mid-nineteen fifties, and output in 1971 reached about 900,000 tons per annum[8] mostly consumed in the form of moulded articles. The catalysts used for these processes fall broadly into two groups. The "Phillips" type catalysts are preformed catalysts of transition metal oxides on a high surface area support materialand the "Ziegler" type catalysts are the reaction product of the combination of transition-metal salts and metal alkyls. The reaction techniques generally employed with these catalysts are fundamentally similar using a hydrocarbon solvent in which the ethylene gas dissolves and which acts as diluent for suspending the catalyst material. The basic difference between the two methods is the physical state of the polymer product. In the one case it is prepared as a molten solution in the hydrocarbon and in the second it precipitates as it is produced to form a slurry suspended in the hydrocarbon. The solution polymerization system can be used with Phillips type processes where the higher temperature and

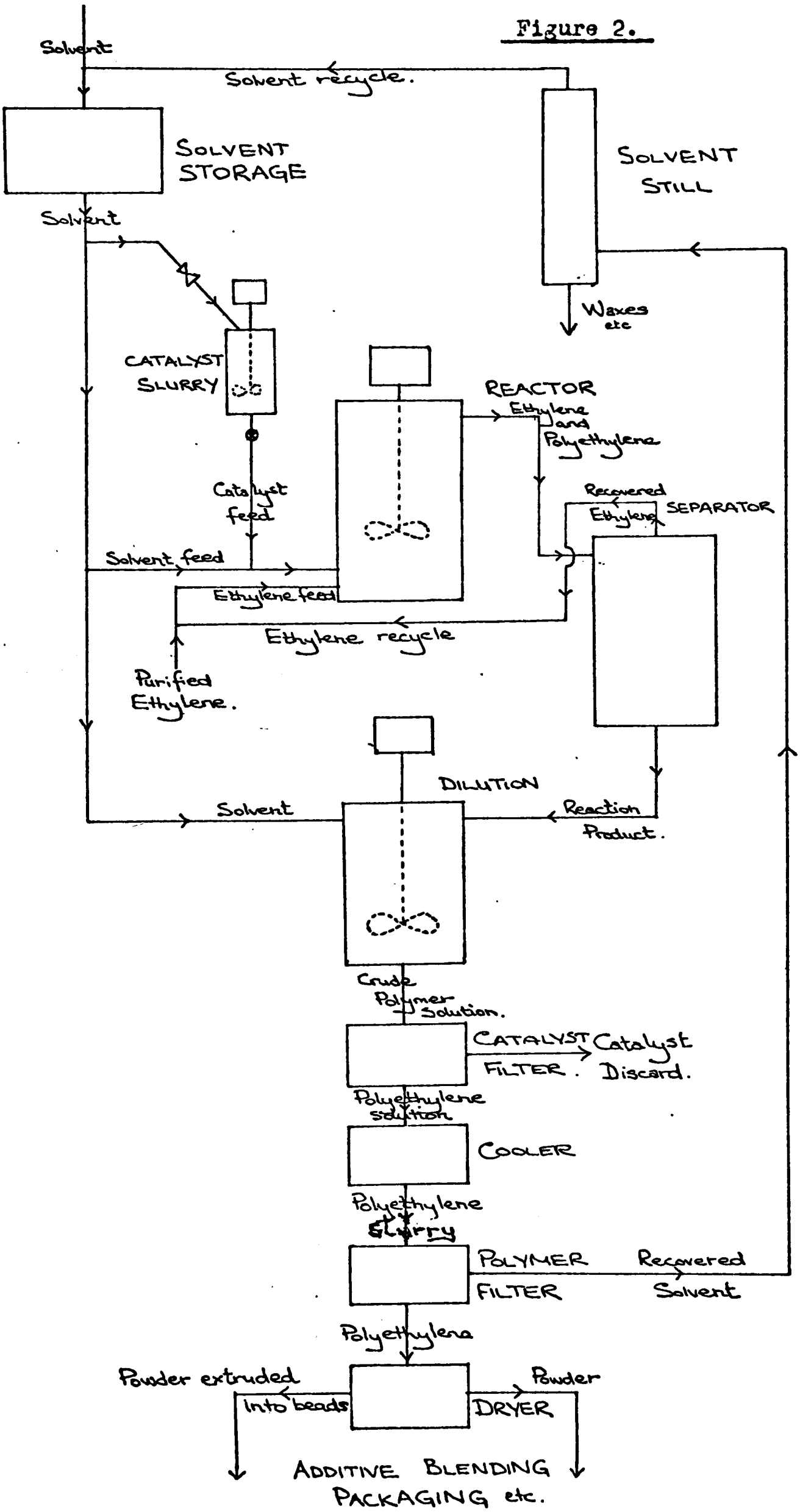
pressure conditions are suitable but the "Ziegler" systems are confined to the slurry process which operates at lower temperatures and pressures.

Phillips type catalyst systems

The Phillips type processes are used particularly in the United States for high density polyethylene synthesis. The catalyst originally devised by the Phillips Petroleum Company[7] consists of about 5% Chromium Oxides (principally CrO_3) on a high surface area silica-alumina (75 - 90% silica) support. It is prepared by impregnating the support with an aqueous solution of a soluble chromium compound such as chromic anhydride or chromium nitrate which when filtered and dried is activated by fluidizing it with air for several hours at 525°C. During activation the chromium ions are maintained as or converted into, the Chromium VI state which is stabilized by the support material.

The Phillips catalyst can be used with several polymerization techniques including fixed bed, moving bed, fluid bed and slurry processes but the latter two are the most popular. Currently in most widespread use is probably the slurry technique which is also used for Ziegler systems and will be outlined when these are discussed later (see Figure 3). The alternative process generally used for Phillips catalysts is the solution process. The process, schematically shown in Figure 2, also uses a hydrocarbon diluent for heat transfer in order to control the reaction temperature. In this method a good solvent for the polymer

Figure 2.



The low pressure solution polymerization method for polyethylene manufacture as used in the Phillips type proocesses.

is used at operating temperatures of 125° - 175°C. and usually at a pressure of 2.5 - 3.0 MNm^{-2} (25 - 30 atmospheres). The process differs little from the slurry technique with the exception of the treatment of the crude product. This is separated from excess monomer which is recycled, then after dilution the catalyst is removed (if necessary by filtration). Solvent is removed either by flashing it off with steam or filtering it off after precipitation of the polymer by cooling. The crude resin is extruded into beads as in the high pressure process.

Alternative catalysts of this type have been prepared by the Standard Oil Company of Indiana , over some years using supported transition metal oxides[9]. The main difference is that these catalysts can be used with a promoter[10] namely an alkali or alkaline earth metal or metal hydride. The catalyst is prepared in a fashion similar to that for the Phillips' catalyst by supporting reduced molybdenum oxide or cobalt molybdate on supports of alumina, titania or zirconia. The promoter is generally present at about 0.1 - 0.5 weight per cent of catalyst. Many alkali and alkaline earth metals, metal hydrides, aluminohydrides borohydrides and metal carbides have been successfully used as promoters[10]. The solution polymerization technique is employed with these catalysts which require temperatures of about 230°C. at a pressure of 7.1 MNm^{-2} (70 atmospheres).

The high density polyethylene material produced by Phillips type catalysts differs only marginally in properties from that produced by Ziegler type processes.

Ziegler type catalyst systems

The Ziegler catalyst systems have been widely developed and used in the European countries. The discovery of this type of catalyst is credited to Professor K. Ziegler[6] and his research school at the Max Planck Institute, Mülheim. However, in earlier work N. Fischer[11] refers to ethylene polymerization by a catalyst mixture of a similar nature (aluminium, aluminium chloride, and titanium tetrachloride) and several British and U.S. patents which stem from the investigations in 1949 of Roedel[12], Pease et al of the Du Pont company also cite combinations of this type. In the middle nineteen fifties, after the Ziegler discovery, intensive work was carried out concurrently by K. Ziegler and Professor G. Natta of the Polytechnic Institute of Milan. The latter investigated the capacity of this type of catalyst for steric control of the propagation sequence involved in the polymerization of higher α-olefins[13] especially with respect to the preparation of "isotactic" polypropylene[14] on the laboratory and commercial scales. The Ziegler systems were later extended to other monomers including conjugated[15] and non-conjugated di-olefins and to copolymers[16] using mixed monomer feeds.

A Ziegler catalyst is usually formed by bringing together in an inert atmosphere a transition metal compound in which the transition metal is in a valency state below its normal maximum (e.g. titanium (III) chloride, vanadium (III) chloride) and an organometallic compound

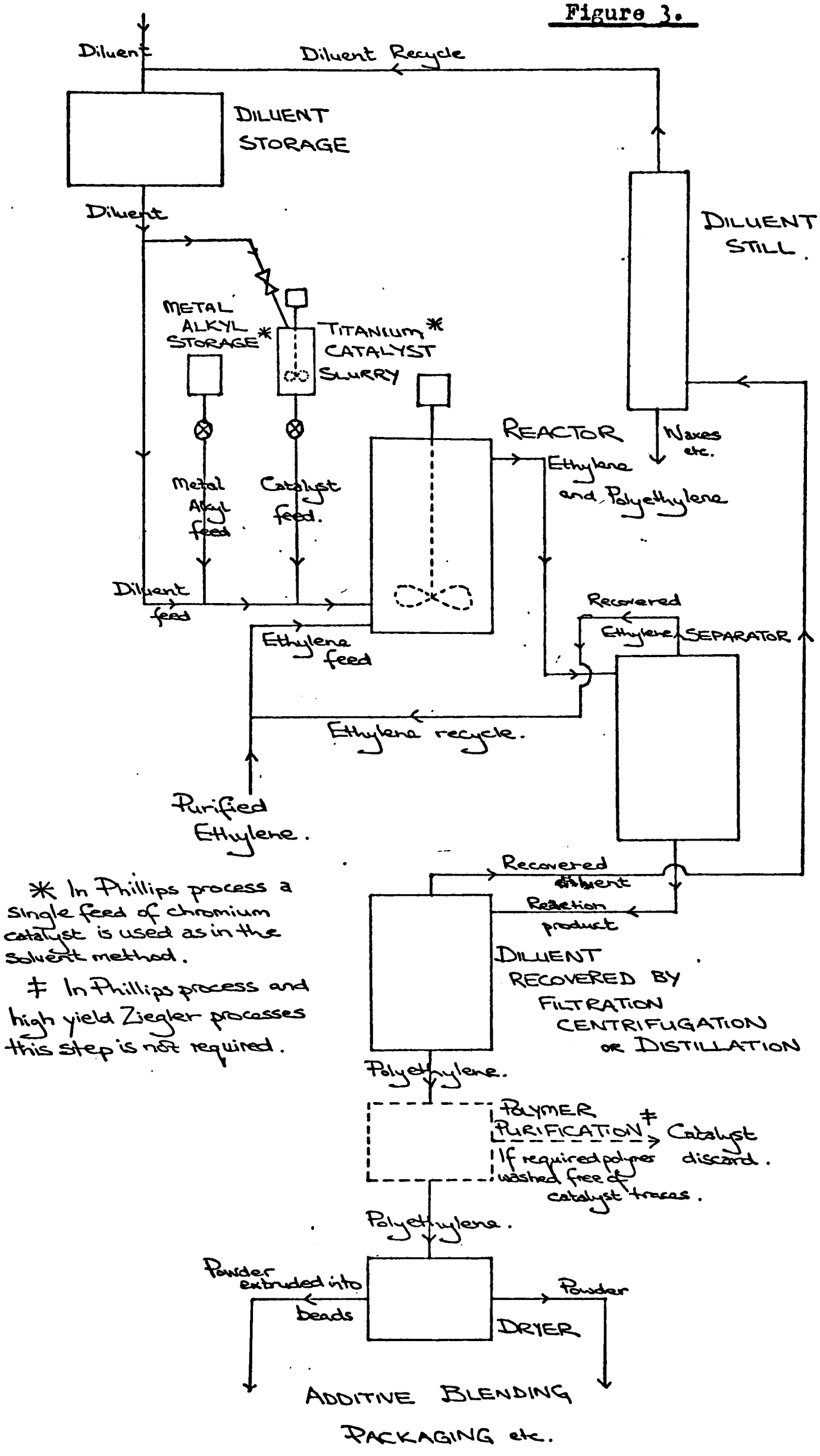
(e.g. aluminium triethyl,aluminium diethyl chloride). The former is normally obtained previously by reduction of a corresponding compound from its normal valency state and is generally thought to be the true catalyst compound. The method of reduction is extremely important, often being the most important single factor in deciding the activity of the catalyst. The latter acts principally as an activator, alkylating the catalytic surface, and also as a scavenger for minor traces of any catalyst poisons.

Ziegler polymerization of ethylene is currently carried out using a slurry of titanium (III) chloride preformed by reduction using an aluminium trialkyl or aluminium dialkyl halide (usually R=Ethyl). The efficiency of the catalyst varies with the nature of the catalyst particles and for this reason care is especially taken over the conditions under which reduction takes place and elaborate techniques have been developed to achieve optimum results. Such reductions produce the βcrystal modification of titanium (III) chloride, when carried out below 70°C.[17]. Although this is an active catalyst for α-olefin polymerization enhanced properties of stereoregulation, particularly in the isotactic polymerization of propylene, are conferred when it is converted to the γmodification which can be achieved by heating above 150°C.[17, 18]. The titanium catalyst is used for polymerization by a slurry process in conjunction with a co-catalyst (normally further aluminium trialkyl or aluminium dialkylchloride). A recent

innovation in the field has been made by Solvay et Cie (Brussels) who have achieved increased activity by supporting their transition metal catalyst on a carrier material. They contend that this gives a capability of 600 Kgm of polymer per gm. of catalyst.

The slurry process for the polymerization of ethylene which is carried out at 0.1 - 1.0 MNm^{-2} (1 - 10 atmospheres) pressure for Ziegler systems is illustrated by Figure 3. When this process is used with the Phillips type catalyst the pressure is typically 2.5 - 3.0 MNm^{-2} (25 - 30 atmospheres) and the reaction temperature about 80° - 100°C. The catalyst is generally suspended in a monomer solvent chosen to be a poor solvent for the polymer and the reaction conditions of less than 100°C. (normally 50° - 80°C.) with Ziegler catalysts ensure that the polymer solubility remains low. During polymerization the polymer is formed as a solid on the catalyst particles and creates a thick slurry of the material in the hydrocarbon diluent. Excess monomer is recycled from the reaction product which is recovered by filtration or flashing off the solvent with steam. The polymer powder can then be dried and may be melted for extrusion into beads as with the alternative systems, if required. Ziegler polymers containing a high proportion of catalyst may also require steps to deactivate the catalyst with alcohol or water. In such cases it may also be necessary to wash out catalyst residues (de-ash) and neutralise the powder before it is dried. On an

Figure 3.



* In Phillips process a single feed of chromium catalyst is used as in the solvent method.

≠ In Phillips process and high yield Ziegler processes this step is not required.

The low pressure slurry polymerization method for polyethylene manufacture as used in both Ziegler and Phillips type processes.

industrial scale the process is usually operated continuously as this eliminates a major batch process limitation which is ,that ultimately the slurry becomes difficult to agitate and to transfer heat through. Also, for the same reason, mass transfer of monomer to catalysts becomes severely hindered.

The high density material produced by either of the low pressure processes has marked differences from the low density product, especially in its physical properties, due to its higher crystallinity; high density (0.94 - 0.96 gm/cm^3) polyethylene has a spherulitic structure which confers a crystallinity of 85 - 95% compared with 40 - 70% for low density material. This is due to an increase in the size of crystallites from less than 20 nm. to 30 - 40 nm.[19]. The higher crystallinity is thus responsible for imparting the higher density and also confers other favourable physical properties, e.g. better rigidity, superior hardness, greater tensile strength, and higher melting point.

<u>The application of ultra-high molecular weight polyethylene in surgical prostheses</u>

The applied objective of this research was to improve upon the physical properties of the type of ultra-high molecular weight polyethylene used for surgical implants, in particular for replacement hip-joints. Initially it was thought that these improvements might be achieved in two major ways:

(a) by improving the physical properties of the polymer through an increase in the molecular weight.

(b) by lowering the content of catalyst residue as a result of using a very active catalyst, and taking meticulous precautions against extraneous impurities.

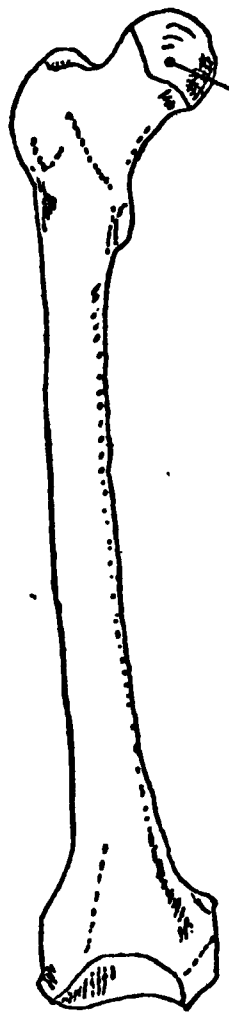
Use of polyethylene in hip prostheses

In recent years considerable development of internal prosthetic devices has occurred, culminating in the total replacement of diseased joints with prostheses using metal/metal, metal/polymer[20, 22] or polymer/polymer bearing surfaces. Few polymers prove suitable in the long term for orthopaedic implant purposes, but high molecular weight high density polyethylene is one of the most successful[21], as a result of its chemical and physical stability in the biological environment.

The mechanical properties of polyethylene, however, limit its application to components not subject to severe bending stresses. In a hip prosthesis (see Figure 4) the intermittent load on the femoral components may occasionally reach 500 Kgf[22] and is typically 100 Kgf for approximately one to two and a half million times in the course of a year. Therefore, these metal/polymer prostheses generally use polyethylene only in the acetabular component, where it is subject only to compressive loads, and austenitic stainless steel for the femoral component where high bending loads are sustained. Such prostheses have a low coefficient of friction which is important in helping to minimize the risk of the

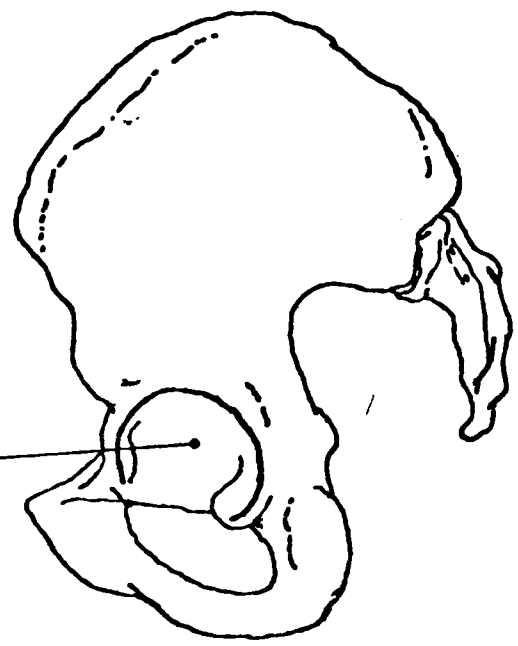
Figure 4.

Right femur
Anterior aspect



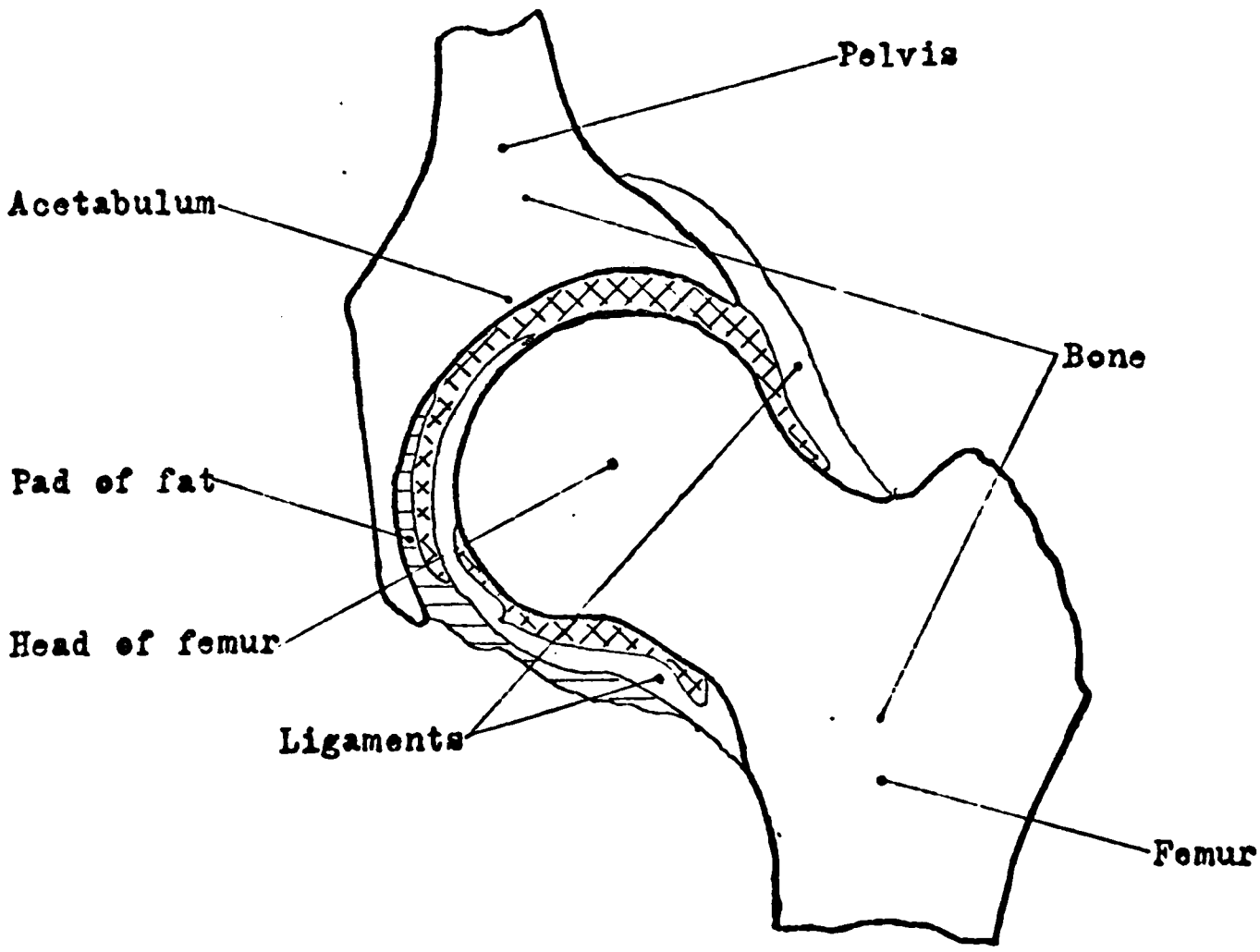
Head of femur

Pelvis
Profile view



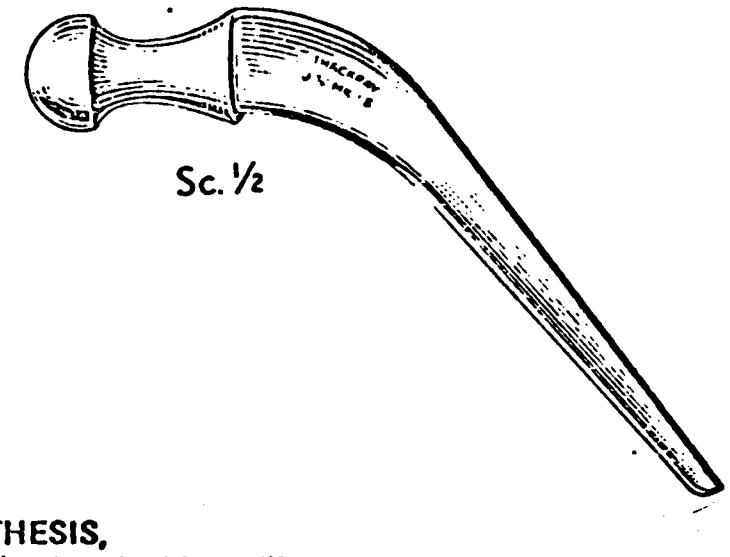
Acetabulum

A section through the hip joint.

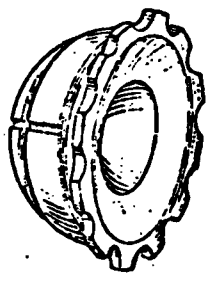


A) The hip joint.

Figure 4.



CHARNLEY FEMORAL PROSTHESIS,
STANDARD, 22.25mm. dia. (⅞") with double radii neck, stainless steel. *



Large

† CHARNLEY ACETABULAR CUP, high density polyethylene, LARGE SIZE, with stainless steel * radiopaque marker and
wire mesh Cement Restrictor, stainless steel.*
(STERILE)

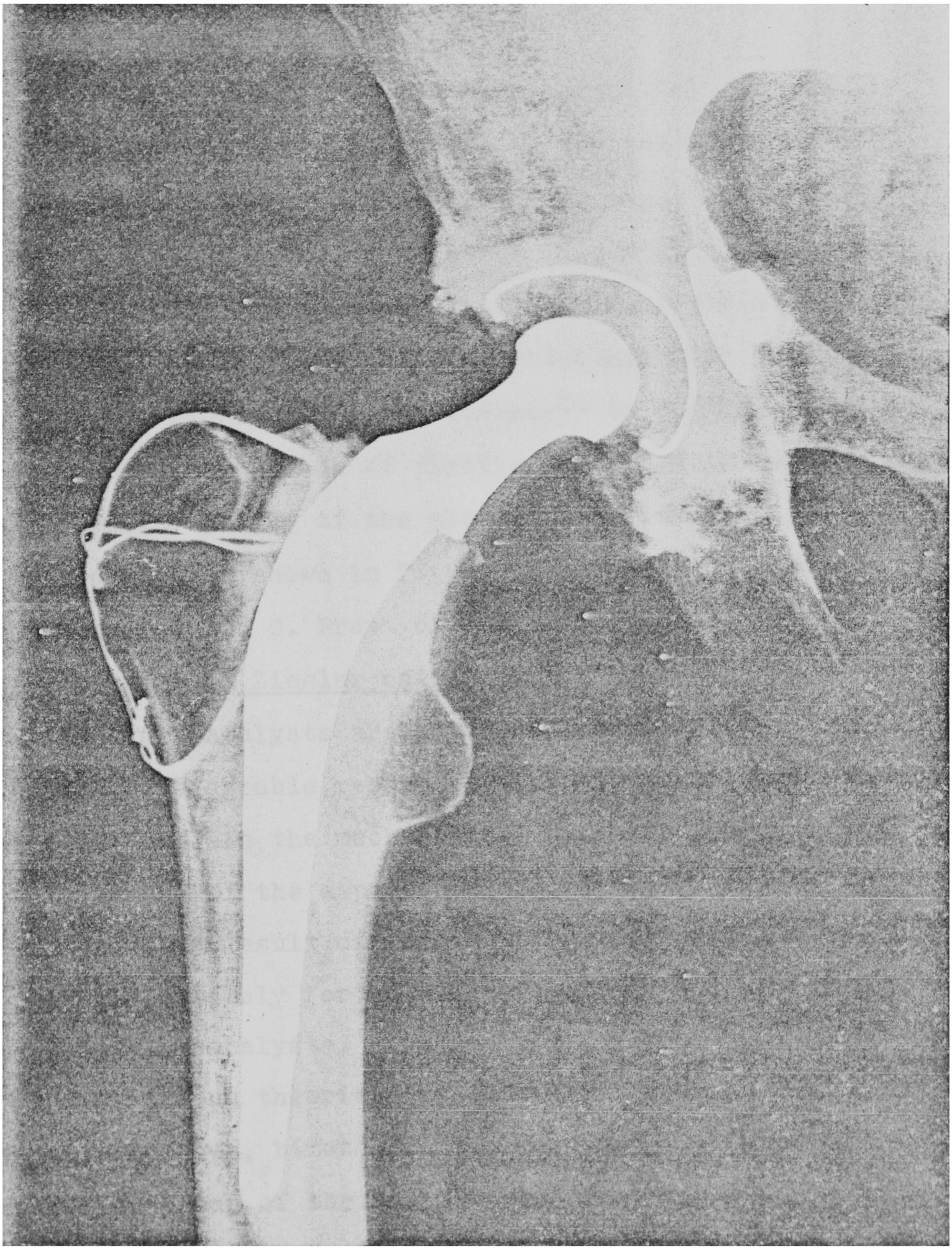
* EN58J Stainless Steel to British Standard Specification, 3531: Part 1: 1968.

† Sterilised by gamma radiation at 2.5 M. Rads.

The Charnley hip prosthesis manufactured by Chas.F.Thackray Ltd. Leeds.

B) The hip prosthesis.

Figure 4.



C) A radiograph illustrating the use of the hip prosthesis.

components loosening and also to give smooth performance. Typically, the alternative metal/metal prostheses have a coefficient of friction about four times[23] greater than those using polyethylene.

The major drawback experienced with this type of prostheses is that the wear rate of the polyethylene component precludes its general use in cases where a long life-time (i.e. in excess of about 25 years) is expected. It is hoped that this property will be improved in the higher molecular weight material which has been produced by this research. There is evidence[24] to suggest that the dry wear resistance of plastic bearings is improved as the molecular weight of the plastic material increases. This property is shown in Figure 5, which is reproduced from work[24] by G. C. Pratt of Glacier Metal Co.

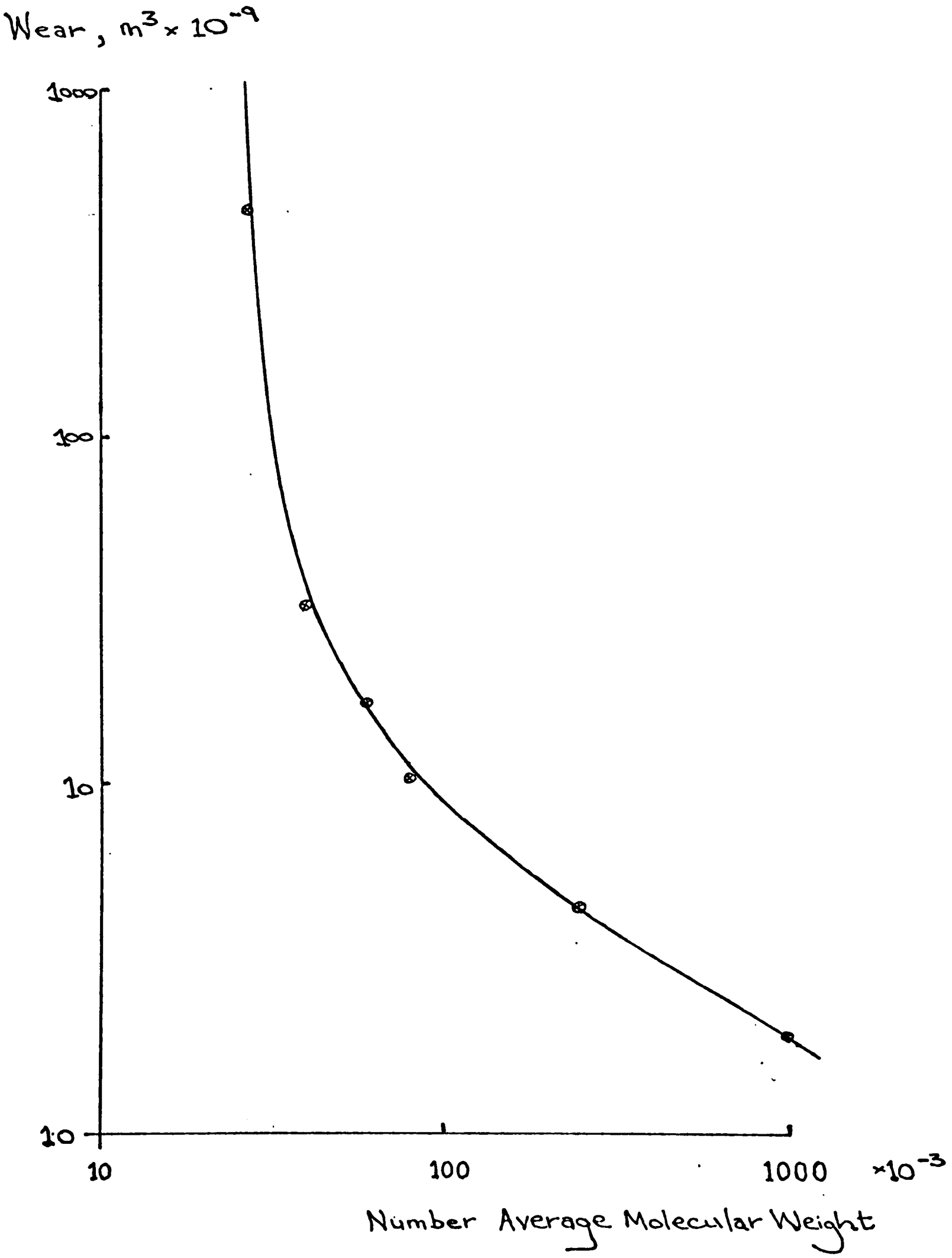
<u>The mechanism of Ziegler catalysis</u>

Ziegler catalysts are immensely complicated systems and even considerable recent developments do not conclusively and fully explain the mechanism(s) by which they operate. However, many of the aspects of the mechanism can be described as a result of recent investigations, and be applied effectively for both heterogeneous and homogeneous Ziegler-type catalysts.

The various theories are generally found to fall into two major groups, bimetallic and mono-metallic mechanisms. The former group of theories is that in which the presence of two metals in the catalyst combination is essential. The latter group is that in which only one metal (the

Figure 5.

Wear of polyethylene after 64 hours under a 7.26 kg. load at 2.06 $m.sec^{-1}$.



The effect of molecular weight on the wear rate of polyethylene.

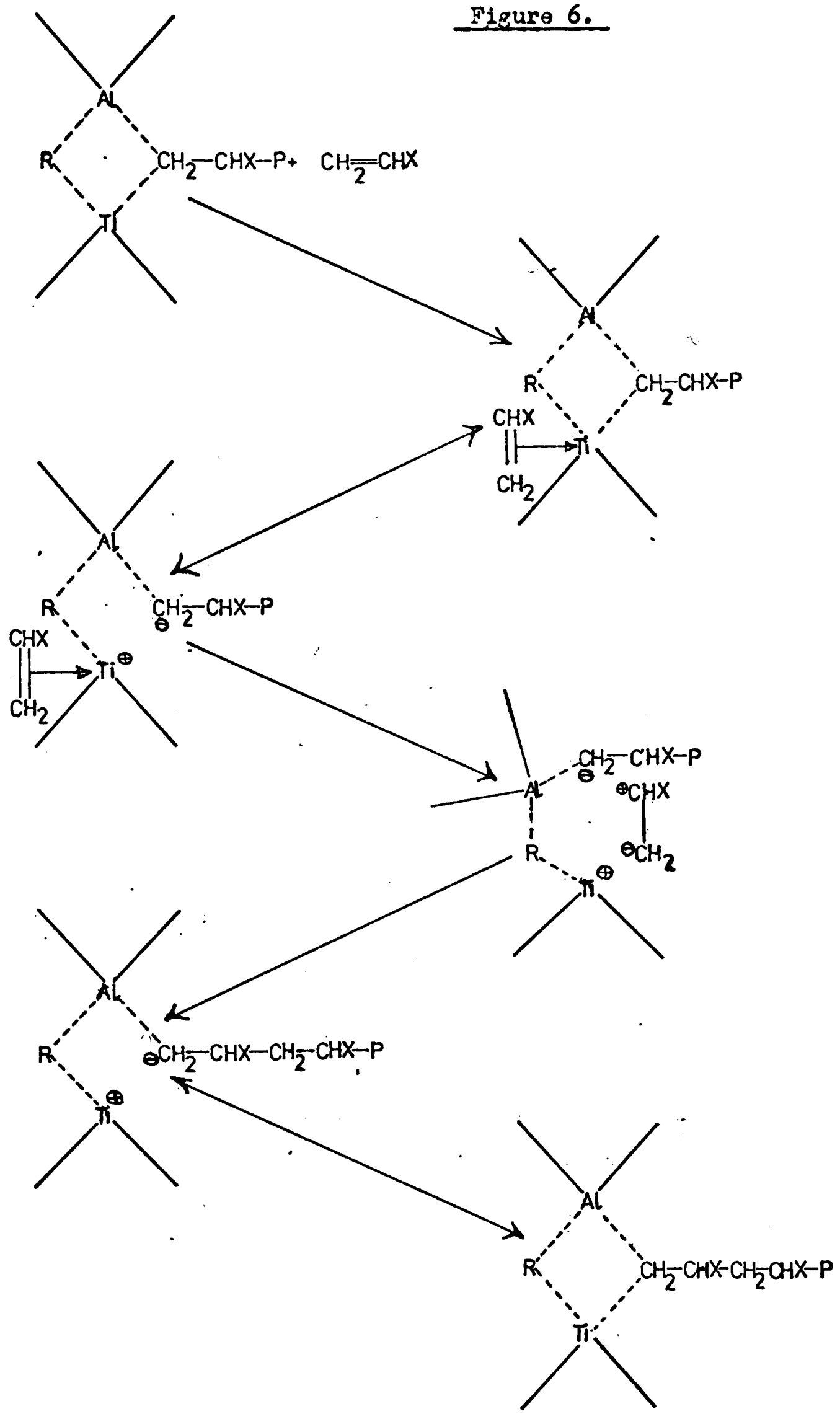
transition metal) is necessary for polymer growth, but a second can be present solely acting as a useful promoter. In the case of bimetallic mechanisms the propagation step employs two metal atoms which may be the same or different elements, whereas a monometallic mechanism involves growth about only one metal centre.

Bimetallic theories

The earlier theories proposed for highly reactive catalyst combinations (e.g. $AlEt_3/TiCl_3$) were usually bimetallic and involved active initiation sites employing a bimetallic complex. One of the most cogent of these mechanisms was proposed by Natta[25] (see Figure 6) and requires two different metal atoms. The complexes involved are located on the surface of the solid catalyst component (e.g. $TiCl_3$). The mechanism as shown is a sequence of insertion reactions in which the driving force for the propagation is the electron deficiency of the complex. The monomer co-ordinates with a titanium atom whilst the titanium-polymer bond is broken; the monomer then associates with an aluminium atom which in the Natta model takes place by polarization of the olefinic π-bond followed by insertion into the aluminium-carbon bond. Various models[26] on this theme have been evolved and conform to certain aspects of the experimental evidence quoted in their support.

A number of radical mechanisms[26] proposed qualify as bimetallic theories. In these polymerization occurs through initiation by a transfer of an electron from an an alkyl radical, transition metal atom or aluminium metal

Figure 6.



Bimetallic mechanism proposed by Natta utilising polymer-bridged structures.

atom to the monomer. Currently evidence can be presented against this type of mechanism[26] and it has fallen into disfavour.

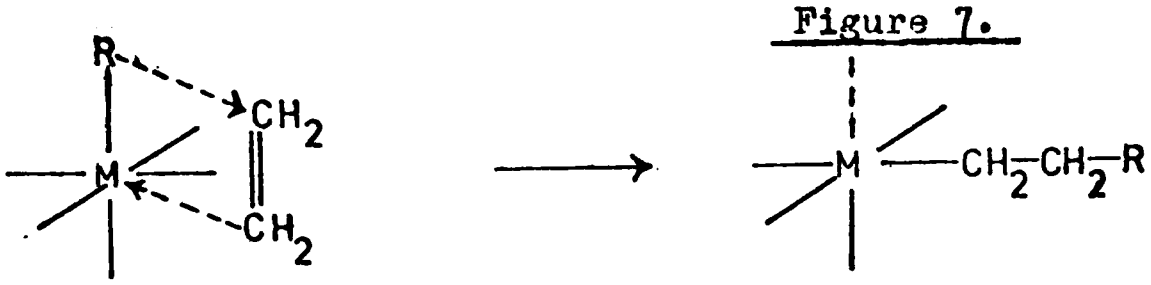
Monometallic theories

This second group of theories is favoured by a greater weight of opinion and an increasing amount of the recent evidence supports this type of mechanism. The first such proposals were made as early as 1956 by Nenitzescu[27], but it was the work of Carol and Carrick[28] which presented the first experimental evidence to support this mechanism. Cossee further developed this model of the polymerization mechanism[29] and described the olefin co-ordination using a molecular orbital treatment[30].

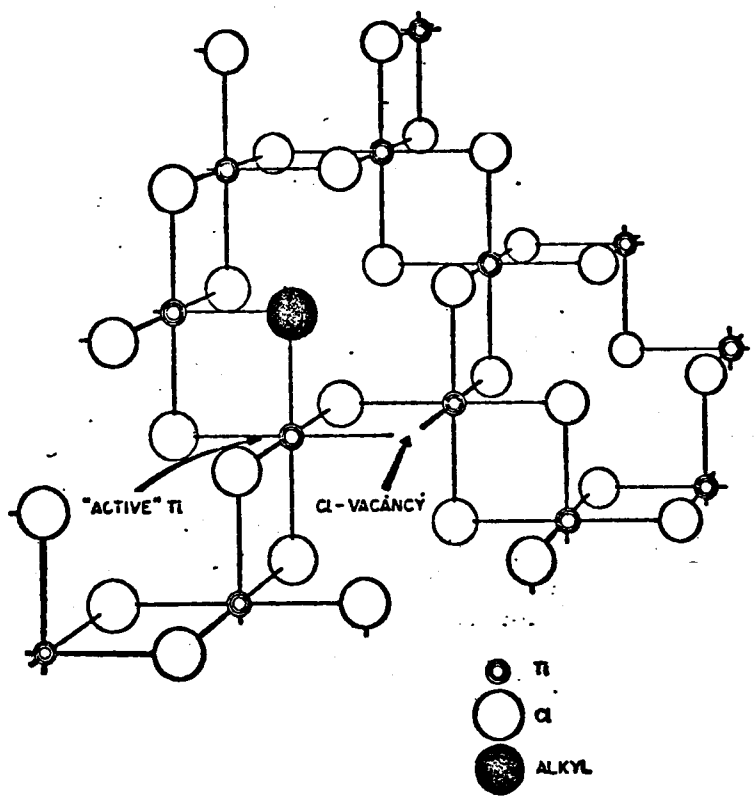
In the monometallic mechanisms the active site is a transition metal atom (e.g. titanium) and a second metal atom (e.g. aluminium) is not directly involved. In such cases, the second catalyst component (e.g. aluminium triethyl) alkylates the reduced transition metal compound (e.g. titanium (III) chloride), forming an active catalyst species (e.g. Ti-Et). Experimental determination of several important polymerization parameters (e.g. Copolymerization reactivity ratio[28]; propagation rate constant[31] in the presence and absence of metal alkyls) support these mechanisms in that they can be related to the properties of the transition metal used but not to the other metal present.

The basic monometallic mechanism originally described by Cossee is given in Figure 7a. The following Figures

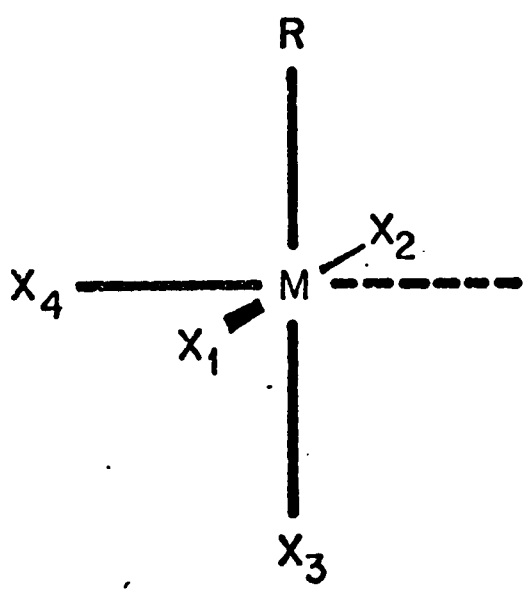
Figure 7.



A) Mechanism for the propagation step as proposed by Cossee.



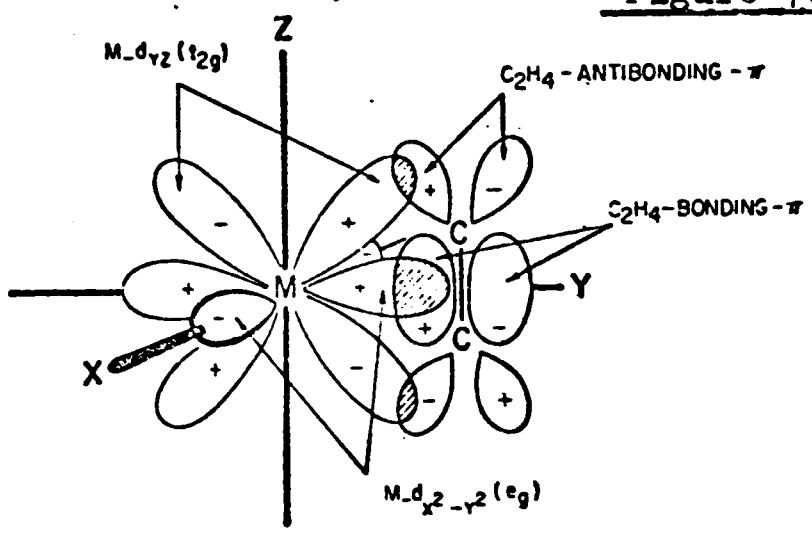
B) One layer of the crystal structure of α-$TiCl_3$ showing the Ti-alkyl bond and the chlorine vacancy forming the "active" centre in the surface.



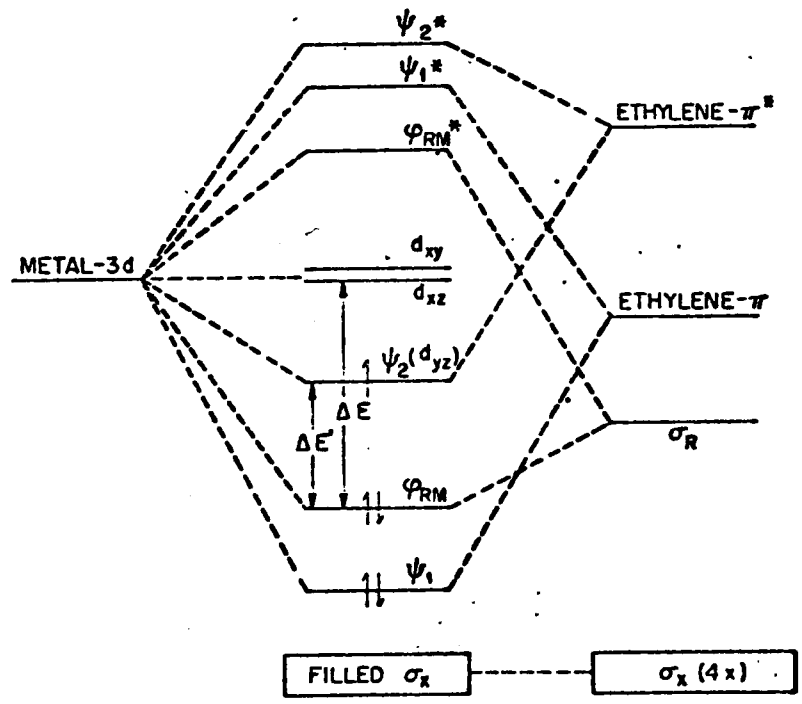
C) The configuration supposed to be the active centre in a Ziegler catalyst. (M = transition metal ion, R = alkyl group(growing polymer chain), X_1-X_4 = anions.)

Diagrams illustrating the Cossee mechanism (I).

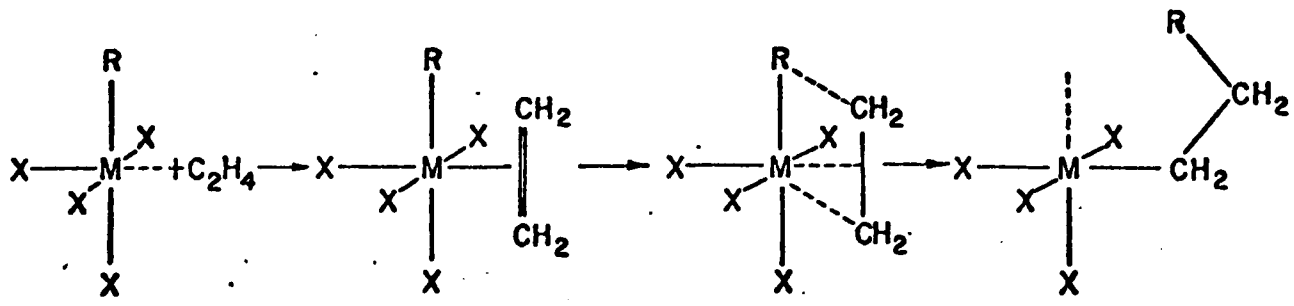
Figure 7.



D) A schematic picture showing the spatial arrangement of the relevant orbitals in a π-bond between a transition metal and ethylene.



E) The molecular orbital energy diagram for the octahedral complex R Ti Cl_4 (C_2H_4).(For reasons of simplicity 4s and 4p orbitals are not taken into account and the Ti-Cl bond is supposed to be 100% ionic.)



F) The complete mechanism sequence proposed by Cossee.

Diagrams illustrating the Cossee mechanism (II).

show:

7b and 7c - the configuration at the active centre,

7d and 7e - the monomer co-ordination and molecular orbital diagram,

7f - the steps involved in the mechanism sequence.

Figure 8 shows the basic features of a modified mechanism recently proposed by Boor[30] in a unified model extending the earlier concepts to the general case.

The Cossee model proposes an active centre consisting of an essentially octahedrally co-ordinated transition element with empty or nearly empty t_{2g} orbitals having in its co-ordination sphere one alkyl group and one vacant octahedral position which must be positioned *cis* to one another. The monomer can then co-ordinate in the vacant position through a "p-π - d-π bond" (See Figures 7d and e). This co-ordination step can be expected to make the transition metal-carbon bond labile and therefore facilitate the mechanism shown in Figure 7a and f .

The Boor[32] model involves two configurations of the active centre (shown as I and II in Figure 8). The particular structure employed depends upon the solubility of the final catalyst material. In heterogeneous systems Boor believes the active centre to be exclusively as in structure I but that structure II may be found in homogeneous systems. The propagation involving the former type of active centre is also shown in Figure 8 as separate co-ordination and insertion steps.

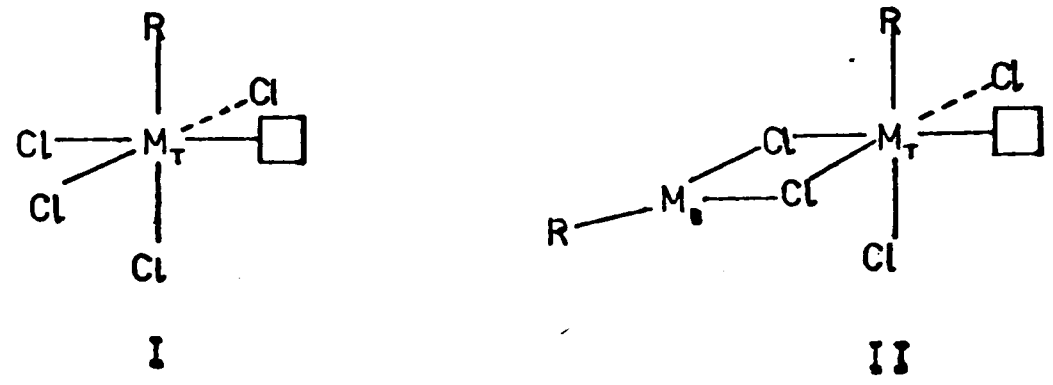
Figure 8.

$M_B R_m + M_T Cl_n \longrightarrow$ Active Ziegler catalyst

where $M_B R_m$ can be $AlEt_3$, $AlEt_2Cl$, $ZnEt_2$, LiBu etc.

$M_T Cl_n$ can be $TiCl_3$, VCl_4, $CoCl_2$ ..... etc.

A) A general scheme for the preparation of Ziegler type catalysts.



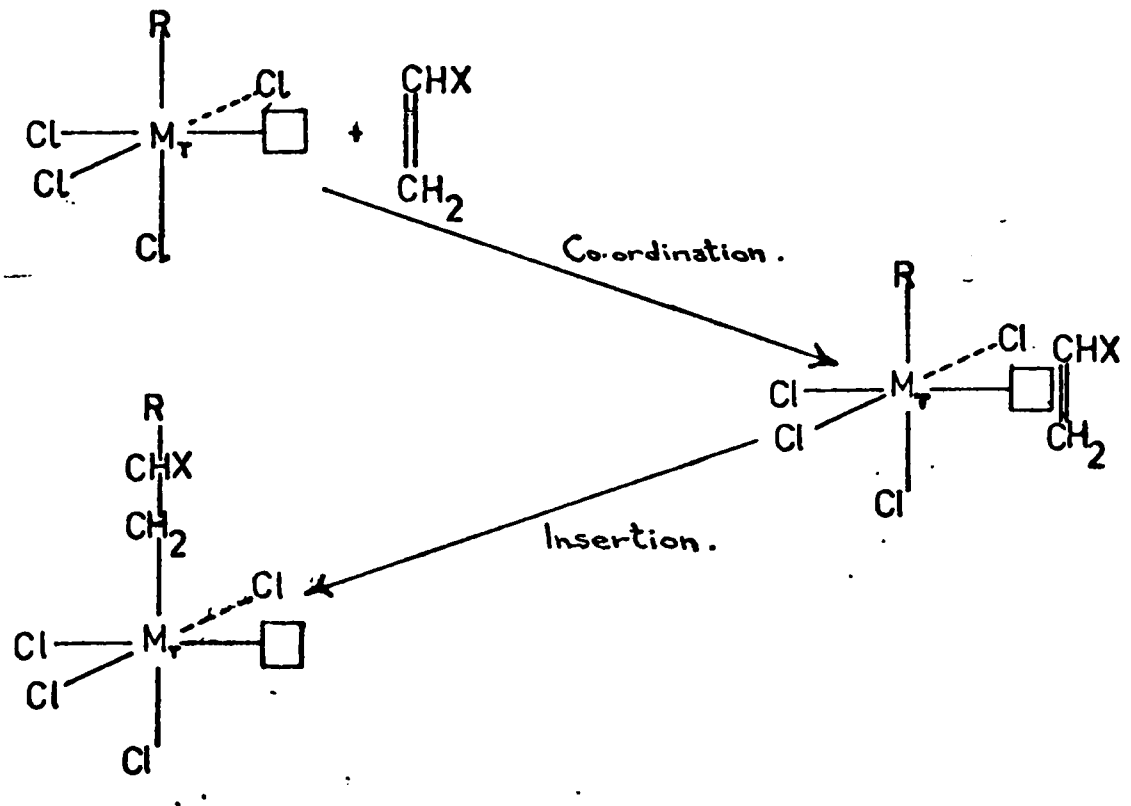
where M_B is a base metal — e.g. Al, Zn.

M_T is a transition metal — e.g Ti, V, Co:

□ is an empty octahedral position through which the defin co-ordinates to the transition metal

R is the alkyl group derived from the metal alkyl.

B) The structures proposed by Boor for the "active" centre in Ziegler catalysts.



C) The mechanism sequence proposed by Boor for the propagation step.

Diagrams illustrating the Boor model.

Magnesium reduced catalysts

The Ziegler catalyst used for the polyethylene preparation in the present work is preformed titanium (III) chloride, activated by an aluminium trialkyl. This differs from conventional catalysts in that the titanium (III) chloride is prepared by reduction of titanium (IV) chloride by an organo-magnesium compound in place of the more usual organo-aluminium reducing agents. This type of catalyst system has been developed by the Shell Research Company Limited[33] and has been used with permission.

CHAPTER 2

THE POLYMERIZATION OF ETHYLENE

The polymerizations were carried out as a batch process using a conventional hydrocarbon diluent technique, and a pure ethylene monomer feed, under either atmospheric pressure or moderately elevated pressures (0.2 - 1.0 MNm^{-2} gauge). An outline of the procedure is given by the schematic representation shown in Figure 9.

Materials

The materials used in this work are outlined below:-

Ethylene

Polymerization grade ethylene monomer was obtained from British Oxygen Co., Ltd., Special Gases Division with the following specification.

Ethylene (% volume)	99.85 minimum
Hydrogen (ppm)	100 maximum
Oxygen (ppm)	5 maximum
Carbon monoxide (ppm)	20 maximum
Other oxygenated compounds (ppm)	10 maximum

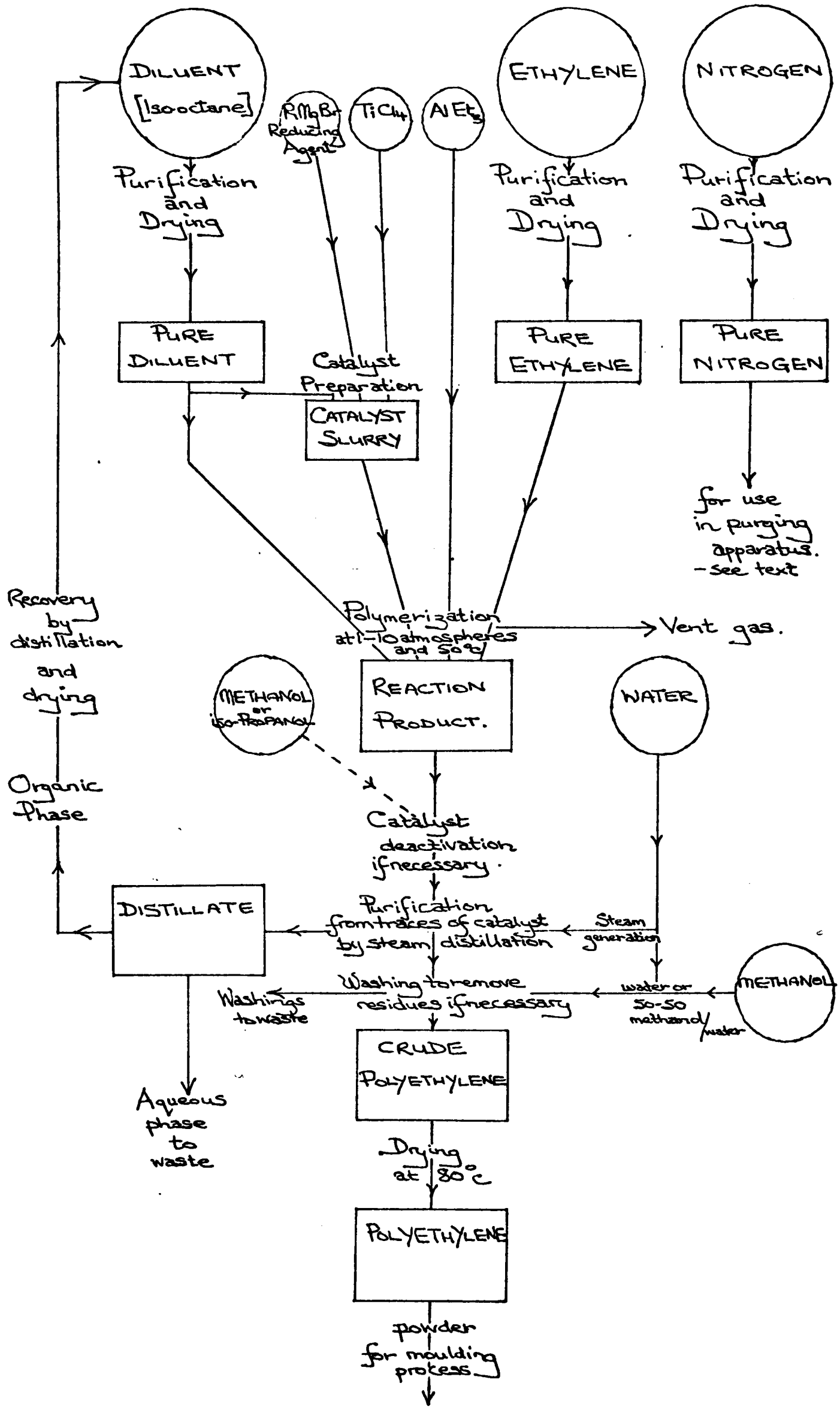
Water dew point $<-40^{\circ}C$. at Atmospheric Pressure

The gas as supplied was purified as described later in the text.

Nitrogen

"White Spot" grade (oxygen-free) Nitrogen was obtained from British Oxygen Co., Ltd. This was purified as described later in the text.

Figure 9.



The experimental scheme for the preparation of high molecular weight polyethylene using a magnesium reduced catalyst.

Iso-octane (2,2,4-trimethyl-pentane)

Iso-octane (99% pure) was obtained commercially, and was distilled before use as outlined later in the text.

Aluminium alkyls

Aluminium triethyl and aluminium diethyl chloride were obtained from Schering A.G., with a specified purity of not <90% by decomposition gas analysis. These were used as supplied or as solutions in pure dry iso-octane (see above). Aluminium diethyl chloride was prepared by reaction of a 1:1 molar ratio of the above reagents.

n-Alkyl halides

n-Dodecyl bromide (B.D.H. Ltd.) was used as supplied. n-Octyl bromide was prepared from n-octanol using the potassium bromide and concentrated sulphuric acid route[34].

Ethers

In catalyst preparations involving etherated Grignard reagents tetrahydrofuran was used. This was distilled from lithium aluminium hydride immediately before use.

Titanium tetrachloride

Titanium tetrachloride (B.D.H. Ltd.) was used as supplied.

Dekalin (dekahydronaphthalene)

Dekalin was employed as the solvent for viscometry determinations. The commercial material was used, after distillation from molten sodium metal, and the addition of 0.1% Ionol as antioxidant. Dekalin used in catalyst preparations contained no antioxidant and was further dried by standing over molecular sieves.

Other reagents

Lithium aluminium hydride, potassium and sodium metals

were used as supplied.

B.A.S.F. Catalyst R3-11 was obtained from Badische Anilin & Soda Fabrik A.G. and the 5 x 3 mm. pellet form used.

Linde molecular sieve type 4A was obtained from British Drug Houses Ltd. and the 1/8" pellet form used. "Ionol" was obtained from Shell Chemical Co., Ltd.

Purification of materials

Iso-octane

The iso-octane was distilled from a drying agent under a blanket of nitrogen in order to minimise traces of water and oxygen present (as shown in the apparatus diagrams Figure 10 and Figure 12). The diluent was added to the distillation flask containing the drying agent at least fifteen hours before it was required, and maintained at about 80°C. for this period whilst being purged with dry nitrogen gas, until immediately before use when it was distilled off into the feed reservoir, the first 10% being rejected.

The drying agent used for purification was lithium aluminium hydride powder in the atmospheric pressure experiments. In the super-atmospheric pressure experiments more accurately reproducible results were obtained by the use of molten sodium-potassium alloy stirred into a suspension as the drying agent. A drying column containing Linde (type 4A) molecular sieve was also inserted immediately prior to the reaction vessel to obtain the minimum level of water impurity.

Used diluent was recovered by steam distillation from the crude polymerization product, and subsequently dried over magnesium sulphate before fractional distillation from lithium aluminium hydride.

Ethylene

The ethylene gas was purified by the system shown in the apparatus diagrams Figure 10 and Figure 12. It consisted of a scrubbing tower containing an activated copper catalyst, B.A.S.F. catalyst R3-11, maintained at 140°C. which removes traces of oxygen, chlorine and sulphur compounds present in the gas stream followed by a drying tower containing Linde (type 4A) molecular sieve pellets at room temperature.

Nitrogen

Nitrogen gas was purified by the same type of system as employed for ethylene (see above).

Preparation of catalyst components

The catalyst chiefly employed in this work was of the magnesium reduced titanium (III) chloride type but an aluminium reduced catalyst similar to the γ-titanium chloride types currently used commercially was prepared for comparative experiments.

Magnesium reduced catalyst

The catalyst components used in this case were aluminium triethyl and preformed titanium (III) chloride prepared by reducing titanium (IV) chloride with a Grignard reagent. The aluminium alkyl was added directly to the polymerization reactor, either as supplied or in a diluted form. Dilution was carried out using purified

iso-octane in an atmosphere of nitrogen.

The alkyl magnesium halide may be one of two types. The first is a Grignard reagent prepared by reaction in a non-solvating solvent (e.g. a hydrocarbon) and the second is prepared by the more usual method, producing an etherated organomagnesium halide[35]. The latter type has been more extensively employed in the current work. The former ether-free Grignard reagents were prepared by the technique of Zakharkin et al[36] in which the magnesium and alkyl halide react in iso-octane yielding a slurry of the desired Grignard reagent partially in solution and partially as undissolved solid. When this technique is used with higher alkyl compounds ($>C_6$) the addition of further solvent and refluxing of the mixture are necessary to adequately dissolve the product. A modified form of the conventional Grignard reagent synthesis was used for the preparation of etherated alkyl magnesium halides. The technique for the preparation of the alkyl magnesium halides used for catalyst reduction is given below.

Preparation of Grignard reagents

This preparative technique is suitable for any alkyl magnesium halide Grignard reagent; the dodecyl magnesium bromide used in this work is given as an example. The Grignard reagent was prepared in apparatus consisting of a 500 cm^3 three necked flask maintained at a uniform temperature in an oil bath heated on a hot-plate. The flask was fitted with a mechanical stirrer, a nitrogen inlet supplied with purified nitrogen, a double surface condenser outlet, fitted with a white oil bubbler, and a tap funnel.

The apparatus was oven dried at 140°C. for twenty-four hours before assembly and then flushed out with nitrogen prior to the addition of 6.8 gms. (0.28 moles) of magnesium powder to the flask. The magnesium was dried *in situ* by stirring at 110°C. - 130°C. for about ninety minutes whilst passing a continuous stream of nitrogen. The apparatus was then cooled to 50°C. - 60°C. and a few drops of neat alkyl halide added from the tap funnel to the stirred magnesium in the flask. The flask was heated in the oil bath at this stage until reaction began as indicated by the appearance of white fumes in the flask. Further alkyl halide was added slowly over a period of about thirty minutes to maintain a smooth reaction at the temperature of initiation until all the dodecyl bromide, 59.9 cm^3 (0.25 moles) had been added. If the reaction is vigorous, the alkyl halide may be diluted with purified iso-octane to control the rate of reflux (e.g. 45 cm^3 for the dodecyl case).

If the reaction is slow then additional heating from the oil bath may be required. In extreme cases where initiation proves difficult, catalytic amounts of an alcohol (e.g. 1% molar ethanol) may be added as outlined by Bryce-Smith[37] in order to facilitate reaction. After completing the addition, heating was continued for a further two hours. At this point more solvent was normally added and the mixture refluxed for an additional two hours to achieve adequate dissolution. In the case of the dodecyl magnesium bromide this was a dilution to

approximately one molar by the addition of 150 cm^3 of iso-octane. On cooling, the mixture separated out into two or three layers. The uppermost clear solution could, with care, be used directly for catalyst preparation (see below) or if necessary filtered or decanted. The residual material consisted of a lower layer of unreacted magnesium and, if present, the middle layer was a slurry of the insoluble solid Grignard reagent.

The above technique produced an ether-free Grignard reagent; the alternative method which was mainly used differed as follows: Where an etherated Grignard reagent was to be prepared, after the initial drops of alkyl halide had been added, the remainder was added as a solution dissolved in the ether (e.g. 20.4 cm^3 (0.25 moles) of tetrahydrofuran in the dodecyl magnesium bromide case). This may be diluted with iso-octane if necessary to regulate the reaction (e.g. 25 cm^3 for dodecyl magnesium bromide), as indicated previously for the ether-free technique.

The strength of the Grignard solutions was estimated as follows. A 5 cm^3 portion was reacted with 10 cm^3 of molar hydrochloric acid. The mixture was heated gently to ensure complete reaction and a little ethanol added to ensure solubility. The molarity was determined by titration against molar sodium hydroxide solution using phenolphthalein indicator.

Preparation of the titanium(III)chloride catalyst component

The titanium (III) chloride catalyst slurry was prepared in apparatus consisting or a 500 cm^3 three-necked

flask equipped with a magnetic stirrer bar and placed in a constant temperature bath. The flask was fitted with a tap funnel, a nitrogen inlet and a white oil outlet bubbler providing a blanket of pure nitrogen within the flask.

A solution containing 6.4 millimoles of the n-dodecyl magnesium bromide together with 54 cm^3 of iso-octane was added to the nitrogen filled flask; all the glassware having been previously dried overnight at 140°C. before assembly. 4.0 millimoles (90 cm^3 of a 45 millimolar solution in iso-octane) of titanium tetrachloride were added slowly from the tap funnel to the vigorously stirred Grignard solution over a period of thirty minutes. In this work the reduction has been carried out at room temperature but other workers report enhanced catalytic properties following reduction at a temperature between -30° and -60°C.[33]. Under all conditions stirring was carried out for not less than three hours after addition was complete. It was found preferable to leave the mixture stirring overnight to ensure the reaction had reached completion. The slurry was diluted by the addition of a further 240 cm^3 of iso-octane and the titanium concentration determined before use by the following method.

A 5 cm^3 sample of the catalyst slurry was syringed into a 250 cm^3 Buchner flask and the mixture evaporated to dryness under a water pump vacuum over a hot oil bath. When the flask had cooled 8 gms. of ammonium sulphate and 20 cm^3 of concentrated suphuric acid were added and the

mixture dissolved by gently warming. The flask was then cooled again before 120 cm^3 of distilled water were carefully added, followed by 20 cm^3 of concentrated hydrochloric acid. The mixture was boiled then cooled prior to the addition of 2gms. of aluminium foil which was allowed to react. As the effervescence subsided the flask was provided with a blanket of nitrogen which was maintained whilst the mixture was brought to the boil until colourless then allowed to cool and finally titrated against 0.02 molar ferric ammonium sulphate solution using ammonium thiocyanate indicator.

Aluminium reduced catalyst

The catalyst components used in this case were aluminium diethylchloride and preformed γ-titanium (III) chloride. The aluminium diethyl chloride co-catalyst was added directly to the reactor as with the aluminium triethyl in the magnesium reduced catalyst case. The γ-titanium (III) chloride was prepared by reducing titanium (IV) chloride with aluminium diethyl chloride and heating the resulting mixture to 150°C. to change it from the β to the γ form.

Preparation of "commercial type" (preformed γ-titanium (III) chloride) catalyst

This catalyst was prepared by a simplification of a method used for the preparation of a commercial γ-titanium (III) chloride catalyst[18]. The catalyst was prepared in the same apparatus as used for magnesium reduced catalysts. A 250 cm^3 flask was cooled to -30°C. after observing the

same precautions as for the magnesium reduced catalyst, (i.e. dry apparatus, nitrogen atmosphere). 42.2 millimoles (52.75 cm^3 of a 0.8 molar solution) of aluminium diethyl-chloride in dekalin were added to the flask and allowed to cool to -30°C. 56.2 millimoles (28.1 cm^3 of a 2.0 molar solution) of titanium tetrachloride were added from the tap funnel to the vigorously stirred aluminium diethyl chloride solution. Throughout the addition which was carried out over a period of one hour the temperature was maintained at -30°C. Upon completion of the addition the mixture was allowed one hour to warm up to 40°C. and then held at that temperature for one hour. The mixture was then heated to 155°C. over the period of an hour, held at 155°C. for one hour, then allowed one hour to cool down to 20°C., whilst being stirred throughout.

When cool, the catalyst was centrifuged and the supernatant liquor decanted off, the residual material was then washed and centrifuged three times and finally made up to 56 cm^3 in dekalin.

The titanium concentration of the slurry was determined by the same technique as used for the magnesium reduced catalysts.

Preparation of ultra-high molecular weight Polyethylene

The techniques of polymerization at atmospheric pressure and for elevated pressures differ very little apart from the details of the apparatus used. The atmospheric pressure reactor system is shown in Figure 10 and

the superatmospheric pressure system in Figure 12. The procedure used for the preparation is described below:

Standard polymerization procedure

a) Atmospheric pressure apparatus

Experiments at atmospheric pressure were carried out in the apparatus shown in Figure 10 using the following procedure. The reaction vessel (see Figure 11) and its ancillaries were thoroughly cleaned, and dried overnight at 140°C. before assembly. When assembled the vessel was immediately flushed out with ethylene to clear standing gas from the pipework by opening taps b, e and f, then flushed with nitrogen by closing tap b and opening tap d and finally evacuated to approximately 25 Nm^{-2} by connecting the vacuum system through tap c after closing taps d and f. During the evacuation the reaction vessel was warmed up to 70°C. by the circulation thermostat.

Meanwhile the diluent was distilled from lithium aluminium hydride into the feed reservoir under a nitrogen stream controlled by taps h and k. After about one hour under vacuum the apparatus was filled with the freshly purified diluent from the feed reservoir through tap p, after closing taps c and e and opening taps n and m. Nitrogen was then admitted through taps d and e until atmospheric pressure was reached, then tap f was opened and the diluent was "sparged" with nitrogen 100 $dm^3 hr.^{-1}$ (controlled by valve g) at a temperature of 70°C. with stirring at approximately 250 r.p.m. for two hours.

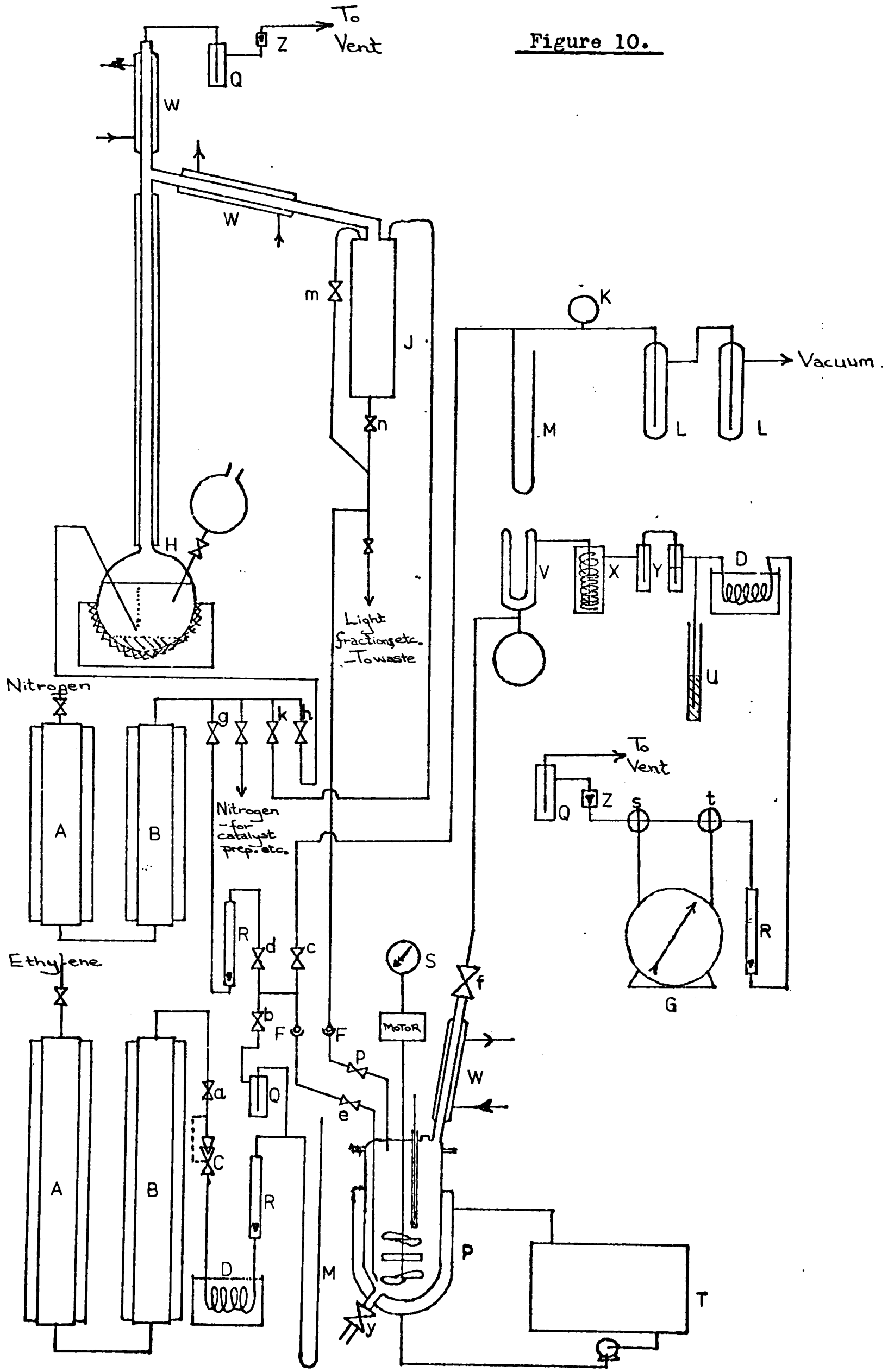
After sparging the diluent and adjusting its volume

KEY TO FIGURES 10 AND 12

A. B.A.S.F. R3-11 catalyst column maintained at 135°C.
B. Linde molecular sieve, type 4A, column.
C. Constant-differential flow controller.
D. Heat exchange coil.
E. Shaw hygrometer sensing element.
F. Ball and socket couplings.
G. Wet type gas meter.
H. Solvent still.
J. Distilled solvent reservoir.
K. McLeod vacuum gauge.
L. Liquid air cooled vapour trap.
M. Manometer.
N. Bursting disc safety valve.
P. Polymerization reactor.
Q. Drechsel bottle vapour trap.
R. Rotameter.
S. Stirrer tachometer.
T. Thermostat bath with circulating pump.
U. Mercury pressure relief tube.
V. "Drikold" condenser.
W. Water condenser.
X. Drechsel bottle vapour trap filled with glass wool.
Y. White oil bubbler.
Z. Non-return valve.

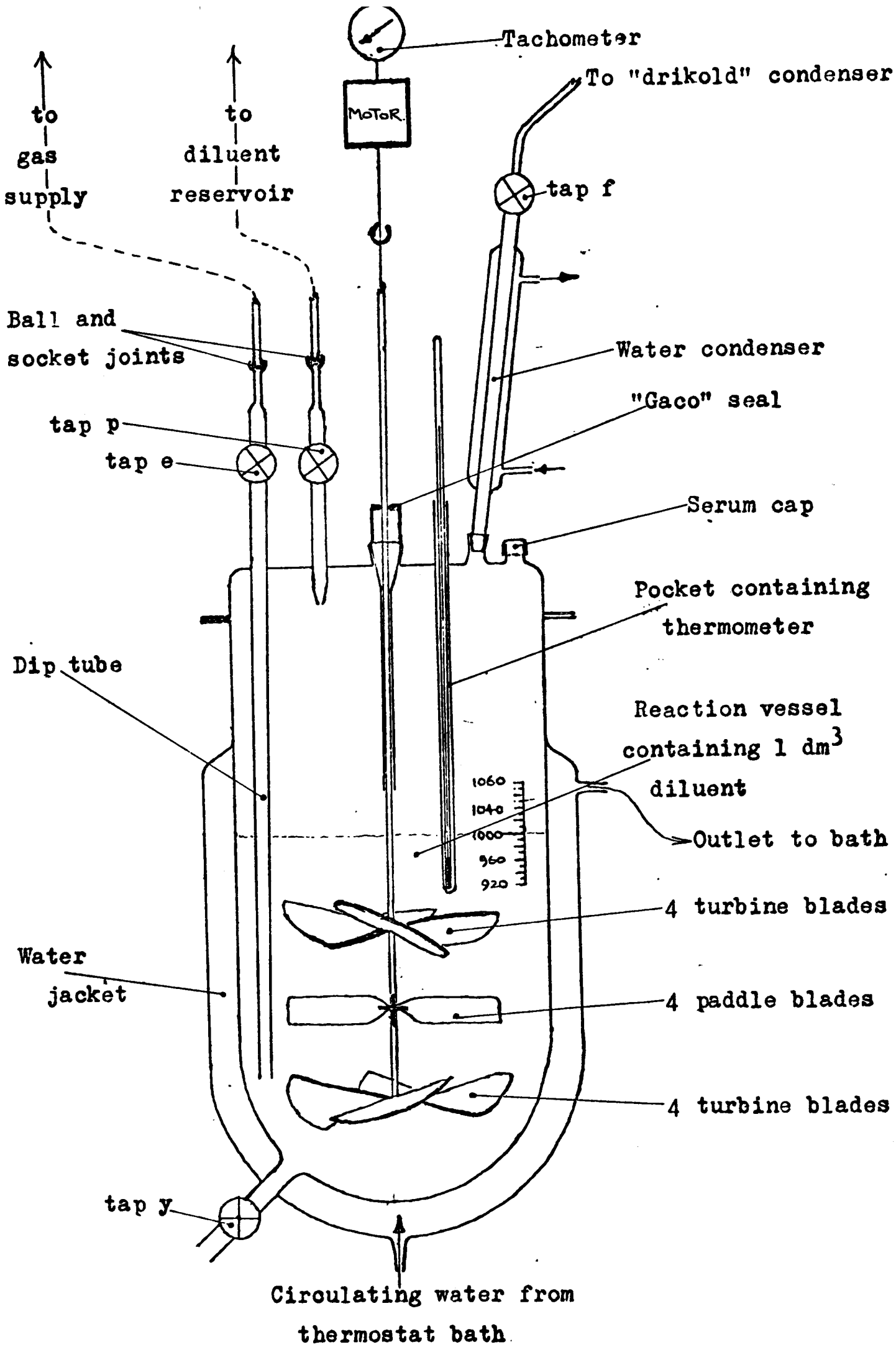
All taps mentioned in the text are labelled with lower case letters.

Figure 10.



The apparatus used for the atmospheric pressure polymerizations.

Figure 11.



The reaction vessel used for the atmospheric pressure polymerizations.

to 1 dm^3 by using tap y, the aluminium alkyl co-catalyst was added by syringe through the serum cap to the unstirred diluent under a nitrogen blanket and the apparatus then allowed to cool to the polymerization temperature. While the apparatus cooled, tap d was closed, tap b opened and the diluent was saturated with ethylene (rate: 50 $dm^3 hr.^{-1}$ controlled by valve a, stirring rate: 250 r.p.m.). When the polymerization temperature was reached after about thirty minutes the stirring speed was raised to 600 r.p.m. The titanium (III) chloride catalyst component was then added in the same fashion as for the aluminium component, and simultaneously the gas meter was started by turning taps s and t.

Polymerizations were generally carried out for three hours and were terminated by closing tap b to stop the ethylene flow and opening tap d to flush the apparatus with nitrogen before finally the titanium was de-activated by exposure to the atmosphere. The crude polymerization mixture was allowed to stand overnight to ensure complete catalyst de-activation and was next steam distilled to remove catalyst residues and volatile organic materials. From the distillate the diluent was recovered for re-cycling, the remainder going to waste. The residue of the steam distillation was filtered off, then washed with two portions of methanol or, in the case of samples containing a high proportion of titanium or aluminium, with two portions of 10% hydrochloric acid solution followed by portions of 50% v/v methanol/water (or methanol

alone) until the filtrate was neutral to litmus. The final powdered material was dried at 80°C. for about 48 hours to constant weight. Viscosity determinations were carried out on this final material.

Experiments were also carried out to determine the viscosity number of the polymer at various times during the reaction. These results were obtained in separate experiments from those involving kinetic determinations but carried out under identical conditions. Samples of about 10 mls. of the reaction mixture were drawn off through tap y at regular intervals. These samples were immediately treated with iso-propanol to quench the reaction and then prepared for viscometry determination as for the bulk samples from the kinetic experiments.

b) Superatmospheric pressure apparatus

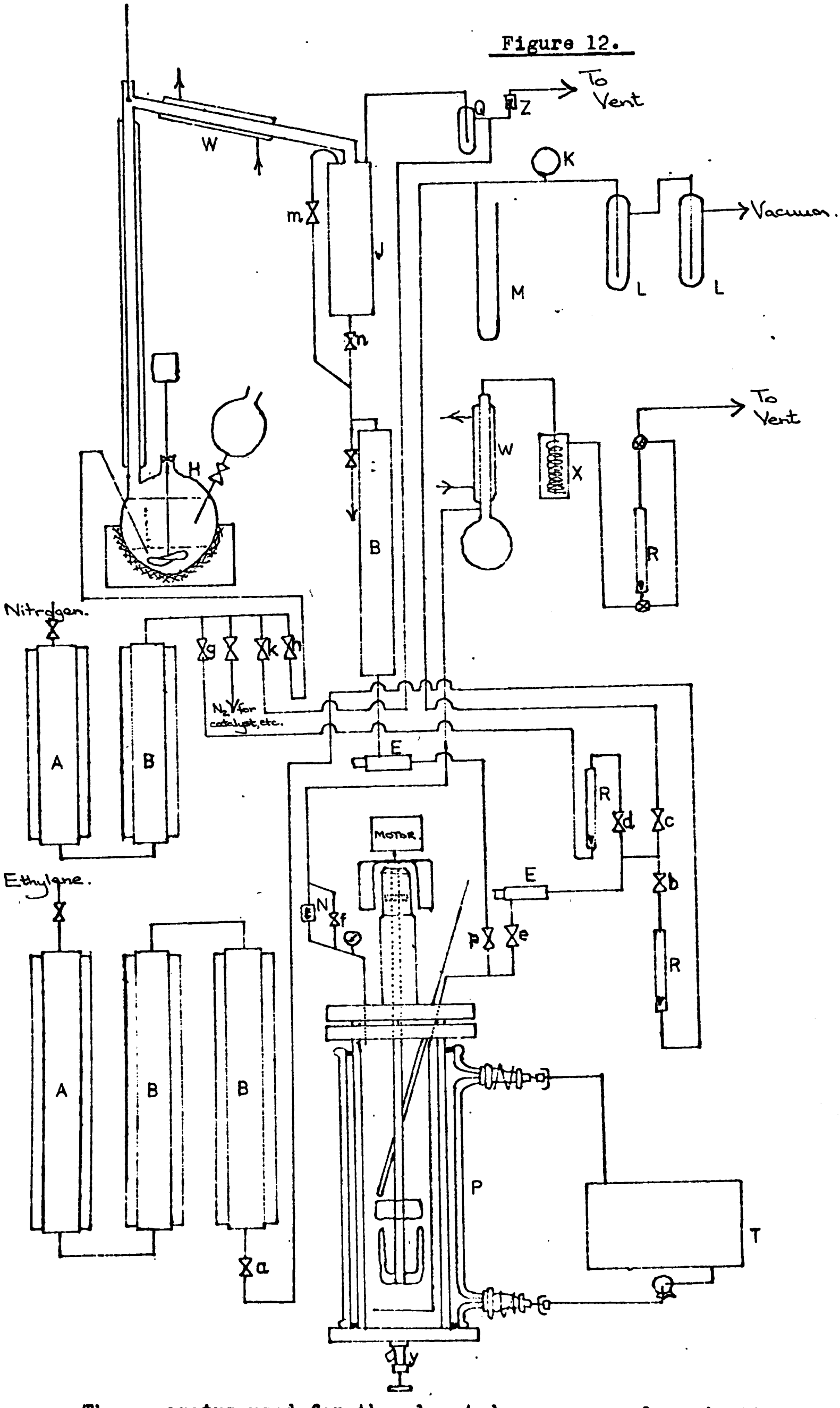
The procedure used for the superatmospheric pressure experiments was basically very similar to that outlined for a) except that the apparatus shown in Figures 12 and 13 was used. The reaction vessel, stirrer assembly, and dip tube were thoroughly cleaned, and dried overnight at 140°C. before assembly. When the warm apparatus was assembled the standing ethylene gas was flushed out by opening taps b, e and f. Nitrogen was used to flush out the ethylene by closing tap b and opening tap d, then the apparatus evacuated by closing tap d and opening tap f. The reaction vessel was evacuated to about 25 Nm^{-2} whilst being warmed to 80°C.

KEY TO FIGURES 10 AND 12

A. B.A.S.F. R3-11 catalyst column maintained at 135°C.
B. Linde molecular sieve, type 4A, column.
C. Constant-differential flow controller.
D. Heat exchange coil.
E. Shaw hygrometer sensing element.
F. Ball and socket couplings.
G. Wet type gas meter.
H. Solvent still.
J. Distilled solvent reservoir.
K. McLeod vacuum gauge.
L. Liquid air cooled vapour trap.
M. Manometer.
N. Bursting disc safety valve.
P. Polymerization reactor.
Q. Drechsel bottle vapour trap.
R. Rotameter.
S. Stirrer tachometer.
T. Thermostat bath with circulating pump.
U. Mercury pressure relief tube.
V. "Drikold" condenser.
W. Water condenser.
X. Drechsel bottle vapour trap filled with glass wool.
Y. White oil bubbler.
Z. Non-return valve.

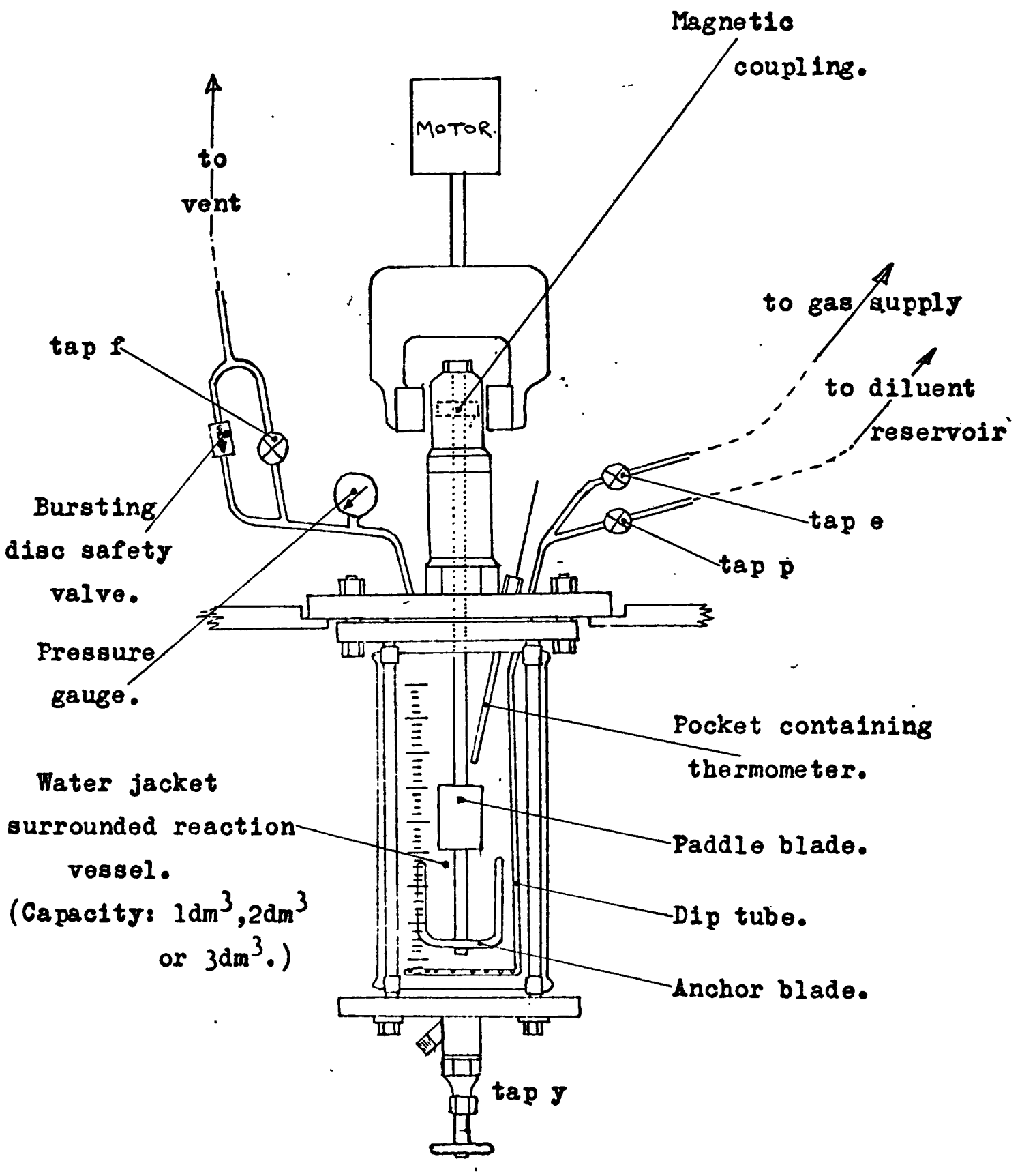
All taps mentioned in the text are labelled with lower case letters.

Figure 12.



The apparatus used for the elevated pressure polymerizations.

Figure 13.



The reaction vessel used for the elevated pressure polymerizations.

At the same time the diluent was distilled off sodium potassium alloy, then let into the feed reservoir under a nitrogen stream from tap h. After about one hour under vacuum the reaction vessel was filled with freshly distilled diluent from the feed reservoir. This was done by closing taps c and e and opening taps m, n and q, then allowing a gentle flow of diluent to percolate through the molecular sieve column by controlling tap p. Meanwhile a nitrogen blanket was provided by opening tap k and the moisture level was monitored to ensure less than 10 ppm of water using a Shaw moisture meter. The pressure was then adjusted to atmospheric by opening taps d and e. The diluent was "sparged" for two hours at a rate of 100 $dm^3 hr.^{-1}$ of nitrogen by opening tap f and controlling the rate by valve g. The temperature was maintained at 80°C. and the diluent stirred at 250 r.p.m.

When the sparging of the diluent was complete, its volume was recorded, and the required amount of aluminium alkyl co-catalyst was added by removing the thermometer pocket and syringing the co-catalyst through the orifice into the unstirred diluent under a nitrogen blanket. The reaction vessel was then allowed to cool to the polymerization temperature whilst the diluent was saturated with ethylene by closing tap d and opening tap e. After half an hour when a steady polymerization temperature was reached, the titanium (III) chloride catalyst component was added in the same way as for the aluminium component.

The thermometer pocket orifice was closed and simultaneously tap f was closed except for a very small bleed, monitored by a rotameter. The stirring speed was increased to 750 r.p.m. and the pressure increased by controlling valve a. Polymerizations were continued for up to three hours or until the reaction rate was minimal. The polymerization was terminated by closing tap b, then releasing the pressure to vent via tap f before flushing the apparatus with nitrogen by opening tap d. Finally the titanium was de-activated by exposure to air by opening the thermometer pocket orifice. Catalyst de-activation was completed by allowing the crude polymer mixture to stand overnight before steam distillation followed by filtration of the residue and washing with two portions of methanol. The final powdered material was dried at 80°C. for about 48 hours to constant weight. The viscosity determinations and moulding tests where applicable were carried out on this final material.

Determination of the Limiting Viscosity Number of Polymer Samples

The polymer samples prepared in this work have been characterised by the determination of the Limiting Viscosity number, $[\eta]$. This can be related to the molecular weight of the sample, M, by the use of an empirical expression of the form $[\eta] = KM^{\alpha}$. Viscometry is a very simple and rapid technique for molecular weight determination and is widely employed in routine applications.

Determinations were made by evaluating the viscosity of a solution of the polymer sample, (η) relative to that

of the pure solvent (η_o). For this purpose capillary viscometers generally of the suspended level type were used. The functions of viscosity employed are expressed conventionally as shown in the table below:-

Definition	Symbol	Name
η/η_o	η_r	Viscosity ratio
$(\eta-\eta_o/\eta_o)$	η_{sp}	Specific viscosity*
$(\eta-\eta_o/\eta_o c)$	$100\ (\eta_{sp}/c)$	Viscosity number
$\lim_{c\to o}\left[\frac{(\eta-\eta_o)}{\eta_o c}\right] = \lim_{c\to o}\left[\frac{\ln(\eta-\eta_o)}{c}\right][\eta]$		Limiting Viscosity number

where c = concentration of polymer solution expressed in grammes of solute per cubic centimetre of solution.

* With this exception terminology as recommended by I.U.P.A.C.[38]

The dimensions of viscosity number and limiting viscosity number (L.V.N.) are $(M^{-1}L^3)$, i.e. cm^3/gm. This is equivalent to 100 times Intrinsic Viscosity, the older term which expresses concentrations in gm/dl and therefore has units of dl/gm.

Experimental procedure

The relative viscosity was determined by measurement of the efflux times of a pure solvent and a polymer solution of known concentration in a capillary viscometer. The determination was carried out in an Ubbelohde suspended level viscometer placed in a thermostat oil bath

at a temperature of 135 ± 0.5°C. using the standard procedure[39]. The technique adopted was as follows:

About 100 cm^3 of the polymer solution was prepared by stirring the polymer powder in dekalin over an oil bath at 150°C. for at least 90 minutes. The solvent was filtered free of dust particles through a glass sinter before use and care was taken to exclude dust from the viscometers. The viscometers were cleaned by standing in chromic acid solution followed by "Decon 75" solution for a period of 24 hours, and finally rinsed in acetone and dried before use. The relative viscosity was found by measuring the efflux time of the pure solvent, dekalin, t_o, and then the time for a 0.02% solution of the polymer sample in dekalin, t, each determination being an average of three consistent measurements of the efflux time. The final result for the relative viscosity was calculated as an average of three separate determinations of different samples of each reaction product.

The Limiting Viscosity Number of the sample and its molecular weight were not actually measured, but were calculated from the average relative viscosity as described later in the text.

* Early viscometry measurements were obtained at 120 ± 0.5°C.

CHAPTER III

RESULTS AND DISCUSSION

THE POLYMERIZATION OF ETHYLENE

Section I - The preparative technique

In order to achieve the applied objectives of this research it was necessary to use a method of preparation of polyethylene which would minimize the metallic residues remaining after catalyst decomposition and maximize the molecular weight of the material. For this purpose a catalyst of markedly improved activity was required so that low catalyst concentrations could be used. The magnesium reduced titanium trichloride system outlined earlier in the text fulfilled this requirement and when used with pure ethylene monomer produced material of high molecular weight. This polymer was prepared as a result of initial investigations carried out on the atmospheric pressure apparatus, followed by further work at elevated pressures where the activity could be increased. As a result of these preparative investigations a quantity (7 kg.) of polymer suitable for moulding into test pieces was produced. This material, which has been moulded in various ways is currently being tested to see if the end product fulfils the applied objectives.

The major difficulty encountered in this preparation was the very stringent precautions necessary to eliminate and exclude catalyst poisons from the apparatus. The exclusion of oxygen and, particularly, of water from the system was the major problem. It was found that when

working at the low catalyst levels ultimately achieved the purification had to be scrupulously carried out (less than 2 ppm impurities) in order to achieve useful results. The methods finally adopted for the purification of the monomer, nitrogen and iso-octane have been outlined in the experimental procedure. Table 3 gives a series of results which illustrate the improvements obtained by taking more stringent steps to exclude catalyst poisons. However, it was necessary throughout the present work to maintain the efficiency of these purification systems in order to obtain reliable results.

Early results obtained during the investigations into the activity of the catalyst system under the standard operating conditions for polymerizations to high conversion, are illustrated in Table 4. It can be seen that there was a fairly large scatter of values in the measured activity parameters. This was attributed to the great difficulty in exact replication of the reaction conditions for any given experiment. Mass transfer[40, 41] appeared to play an important part in this respect especially when the reaction slurry reached high viscosity conditions during the later stages of the reaction. Under such conditions it was found that the rate of ethylene consumption is markedly dependent upon the stirring speed and considerable effort was spent in trying to improve the efficiency of the stirrer devices used in each of the reaction vessels, but with thick slurries ($\sim$ 20%) the problem was not entirely eliminated.

Table 3

Early results from preparative experiments showing improvements made by lowering the reagent impurity levels

Run No.	Temperature, °C.	Pressure, Nm^{-2} gauge x 10^{-5}	Concentration, mmoles		Slurry, % weight	Yield, gms.	Activity, $kg.gm.^{-1}$ †	Specific activity $kg.gm.^{-1} hr.^{-1} atmos^{-1}$ †	Bulk density $gm.cm^{-1}$	Viscosity number, cm^3gm^{-1} x 10^{-2} **
			$TiCl_3$	$AlEt_3$						
OP.1	50	Atmospheric	0.67	4.9	27	188.3[a]	2.4	0.8	0.32	13*
OP.2	"	"	0.67	4.9	25	170.8[a]	2.2	0.6	0.30	13*
OP.3	"	"	0.13	0.98	11	66.0[a]	4.3	1.3	0.28	23*
OP.6	"	"	0.10	1.5	14	113.2[b]	7.3	1.8	0.32	19*
OP.7	"	"	0.10	1.5	19	164.3[b]	10.2	2.0	0.18	19
OP.8	"	"	0.03	1.5	17	144.5[b]	31.5	5.7	0.20	21*
OP.13	"	"	0.03	1.8	20	171.8[b]	37.4	9.4	0.22	22*
OP.14	"	"	0.03	3.7	19	163.4[b]	35.6	7.1	0.22	19*
OP.43	50	2.0	0.04	1.0	10	60.3[a]	13.0	1.4	0.23	18

CONTD....

-44-

Table 3 (Contd.)

Run. No.	Temperature, °C.	Pressure, Nm^{-2} gauge x 10^{-5}	Concentration, mmoles		Slurry, % weight	Yield, gms.	Activity, kg.gm.$^{-1}$ ‡	Specific activity, kg.gm.$^{-1}$ hr.$^{-1}$ atmos^{-1} †	Bulk density gm.cm^{-1}	Viscosity number, cm^{3}gm^{-1} x 10^{-2} **
			$TiCl_3$	$AlEt_3$						
OP.45	50	2.0	0.04	1.9	11	66.3[a]	14.3	2.4	0.21	20
OP.46	"	"	0.08	14.7	37	307.0[a]	33.3	2.8	0.29	13
OP.48	"	"	0.02	10.1	21	144.0[a]	62.3	6.9	0.26	18
OP.50	"	"	0.02	8.4	11	72.9[a]	31.5	4.2	0.25	7
OP.59	"	"	0.04	2.0	21	269.4[c]	29.4	2.8	0.18	25
OP.61	"	"	0.02	0.5	21	271.0[c]	59.1	4.9	0.22	5
OP.62	"	"	0.008	0.5	7	181.0[d]	39.5	3.9	0.19	7
OP.66	"	9.0	0.002	0.4	16	220.2[c]	470.0	18.8	0.20	31
OP.67	"	"	"	0.5	23	324.0[c]	689.6	19.7	0.21	27

NOTES:

‡ The activity of the catalyst is expressed as Kg. polyethylene produced per gm. of $TiCl_3$ catalyst component.

† The specific activity of the catalyst is expressed as Kg. polyethylene produced per gm. of $TiCl_3$ catalyst component per hour per atmosphere of ethylene pressure [1 atmosphere = 1.0×10^5 $Nm.^{-2}$].

Table 3 (Contd.)

** Viscosity number is quoted for 0.02% solutions in dekalin at 135°C.

* Determination of viscosity number in these cases at 120°C.

An octyl magnesium bromide Grignard reagent was used for the preparation of the titanium (III) chloride used in these experiments.

a - 750 cm^3 scale experiment, b - 1,000 cm^3 scale experiment, c - 1,500 cm^3 scale experiment, d - 3,000 cm^3 scale experiment.

-46-

Table 4

Early results from preparative experiments in which polymerization is taken to high conversion

Run No.	Temp. °C.	Pressure Nm^{-2} gauge $\times 10^{-5}$	Concentration mmoles		Slurry %weight	Yield, gms.	Activity $Kg.gm.^{-1}$ †	Specific activity, $Kg.gm^{-1}hr.^{-1}atmos^{-1}$ †	Bulk density $gm.cm^{-1}$	Viscosity number $cm^3gm.^{-1}\times 10^{-2}$ **
			$TiCl_3$	Al Alkyl §						
OP.34	30	Atmospheric	0.03	2.9 TEA	14	102.7[b]	22.2	5.5	0.21	27
OP.36	"	"	0.04	4.4 TEA	11	63.6[a]	13.8	3.4	0.18	25
OP.38	50	Atmospheric	0.03	0.7 TEA	18	154.9[b]	33.5	8.4	0.24	20
OP.39	"	"	0.03	1.4 TEA	20	177.8[b]	38.4	14.4	0.26	19
OP.40	"	"	0.03	0.7 TEA	16	134.9[b]	29.2	7.3	0.23	23
OP.42	"	"	0.03	0.7 TEA	31	311.4[b]	67.3	18.8	0.27	19
OP.21	30	Atmospheric	0.09	1.8 TNOA	0.8	5.4[b]	0.4	0.1	-	24*
OP.15	50	Atmospheric	0.03	2.2 TNOA	1.5	10.0[b]	2.2	0.4	-	23*
OP.16	"	"	0.03	1.1 TNOA	0.7	4.7[b]	1.0	0.2	-	29*
OP.19	"	"	0.03	2.2 TNOA	2.0	13.2[b]	3.0	0.7	-	24*
OP.20	"	"	0.06	3.5 TNOA	2.0	17.3[b]	2.0	0.5	-	27*
OP.32	"	"	0.03	4.4 TNOA	2.0	13.9[b]	3.0	0.8	-	29
OP.30	70	Atmospheric	0.04	2.8 TNOA	25	179.9[a]	38.9	9.7	0.23	18

CONTD....

-47-

Table 4 (Contd.)

Run No.	Temp. °C.	Pressure Nm^{-2} gauge x 10^{-5}	Concentration mmoles		Slurry %weight	Yield gms.	Activity $Kg.gm^{-1}$ ‡	Specific activity, $Kg.gm^{-1}hr.^{-1}atmos^{-1}$ †	Bulk density, $gm.cm^{-1}$	Viscosity number, cm^3gm^{-1} x 10^{-2} **
			$TiCl_3$	Al Alkyl§						
OP.37	30	Atmospheric	0.04	7.9 TiBA	1.3	6.7[a]	1.4	0.5	-	18
OP.65	50	9.0	0.002	0.5 TEA	24	352.9[c]	753.2	25.1	0.21	25
OP.66	50	"	0.002	0.4 TEA	16	220.2[c]	470.0	18.8	0.20	31
OP.67	50	"	0.002	0.5 TEA	23	324.0[c]	689.6.	19.7	0.21	27
OP.68	50	"	0.002	0.5 TEA	14	149.0[c]	317.2	15.9	0.21	25
OP.69	50	"	0.002	0.26 TEA	18	219.6[c]	467.4	12.5	0.19	26
OP.70	50	"	0.002	0.27 TEA	25	314.3[c]	669.0	53.5	0.18	23

NOTES: § Type of aluminium alkyl co-catalyst indicated as follows:-

TEA = Triethyl aluminium

TNOA = Tri-n-octyl aluminium

TiBA = Tri-iso-butyl aluminium

‡ The activity of the catalyst is expressed as Kg. polyethylene produced per gm. of $TiCl_3$ catalyst component.

† The specific activity of the catalyst is expressed as Kg. polyethylene produced per gm. of $TiCl_3$ catalyst component per hour per atmosphere of ethylene pressure [1 atmosphere = 1.0 x 10^5 Nm^{-2}].

-48-

Table 4 (Contd.)

** Viscosity Number is quoted for 0.02% solutions in dekalin at 135°C.

* Determination of viscosity number in these cases at 120°C.

An octyl magnesium bromide Grignard reagent was used for the preparation of the titanium (III) chloride used in these experiments.

Scale of reaction: a - 750 cm^3, b - 1,000 cm^3, c - 1,500 cm^3.

-49-

Table 5

Results from preparative experiments in which material for moulding tests was produced

Run No.	Concentration mmoles		Slurry % weight	Yield, gms.	Activity $Kg.gm^{-1}$ †	Specific activity $Kg.gm^{-1}hr^{-1}atmos^{-1}$ †	Bulk density, $gm.cm^{-1}$	Viscosity number, $cm^3gm^{-1} \times 10^{-2}$ **
	$TiCl_3$	$AlEt_3$						
OP.88	0.002	0.15	23	308.9[c]	656	29.2	0.24	28
OP.89	0.002	0.16	23	549.6[d]	585	24.2	0.24	26
OP.90	0.002	0.17	19	222.5[c]	478	14.0	0.24	25
OP.94	0.002	0.30	17	208.0[c]	444	15.0	0.24	26
OP.95	0.002	0.14	17	220.5[c]	470	16.0	0.22	27
OP.96	0.002	0.15	25	349.2[c]	740	40.2	0.25	25
OP.97	0.002	0.16	24	624.8[d]	664	37.9	0.24	25
OP.100	0.002	0.15	17	208.2[c]	444	36.4	0.15	28
OP.101	0.002	0.15	19	474.4[d]	505	33.3	0.16	31
OP.102	0.002	0.15	20	517.0[d]	555	18.4	0.19	32
OP.107	0.002	0.15	13	431.9[d]	460	15.3	0.22	26
OP.108	0.002	0.15	12	283.8[d]	300	10.0	0.19	29

CONTD....

Table 5 (Contd.)

Run No.	Concentration, mmoles		Slurry % weight	Yield, gms.	Activity, Kg.gm^{-1} †	Specific activity, Kg.gm^{-1}hr^{-1} atmos †	Bulk density, gm.cm^{-1}	Viscosity number, cm^{3}gm^{-1} x 10^2 **
	$TiCl_3$	$AlEt_3$						
OP.109	0.002	0.25	21	559.6[d]	594	19.8	0.24	30
OP.112	0.002	0.15	31	607.9[d]	865	30.6	0.28	23
OP.113	0.002	0.15	23	615.5[d]	655	21.8	0.25	26
OP.119	0.002	0.14	20	546.4[d]	580	19.9	0.25	30
OP.120	0.002	0.14	14	366.6[d]	390	13.4	0.29	29
OP.121	0.002	0.15	18	458.7	487	16.3	0.26	27
The polymer prepared in the experiments quoted in this table between numbers OP.88 and OP.121 has been used for the current moulding tests.								
DP.12	0.002	0.26	22	272.5[c]	606	24.2	0.22	31
DP.13	0.002	0.13	23	237.8[c]	528	28.8	0.21	29
DP.14	0.002	0.13	20	295.5[c]	656	32.8	0.22	30
DP.15	0.002	0.15	17	207.2[c]	460	15.3	0.24	31

CONTD....

-51-

Table 5 (Contd.)

Run No.	Concentration, mmoles		Slurry % weight	Yield, gms.	Activity, $Kg.gm^{-1}$ †	Specific activity, $Kg.gm^{-1}hr^{-1}$ atmos †	Bulk density $gm.cm^{-1}$	Viscosity number, $cm^3gm^{-1} \times 10^2$ **
	$TiCl_3$	$AlEt_3$						
DP.18	0.002	0.15	27	313.9[c]	954	42.4	0.27	-
DP.19	0.0008	0.14	24	347.0[c]	1687	106.5	0.24	19
DP.20	0.0008	0.14	21	587.5[c]	14,300	450.9	0.27	30

All the experiments in this table were carried out at 9.0×10^5 Nm^{-2} gauge pressure and 50°C.

‡ The activity of the catalyst is expressed as Kg. polyethylene produced per gm. of $TiCl_3$ catalyst component.

† The specific activity of the catalyst is expressed as Kg. polyethylene produced per gm. of $TiCl_3$ catalyst component per hour per atmosphere of ethylene pressure [1 atmosphere = 1.0×10^{-5} Nm^{-2}].

** Viscosity number is quoted for 0.02% solutions in dekalin at 135°C.

In the experiments prefixed OP. an octyl magnesium bromide Grignard reagent was used for the preparation of the titanium (III) chloride whilst in those prefixed DP. a dodecyl magnesium bromide was employed.

Scale of reaction: c - 1,500 cm^3, d - 3,000 cm^3

The preparative investigations illustrated the effect of pressure upon viscosity number of the polymer produced by this catalyst system as shown by Figure 14. This confirms an increase in molecular weight with increasing ethylene pressure as previously observed with similar systems[42]. It was also shown that the catalyst is very susceptible to poisoning by traces of aluminium alkoxide formed by the decomposition of the aluminium trialkyl. Great care was subsequently taken to avoid this, as such decomposition could only be detected by analysis of the aluminium trialkyl.

The results and conditions used for the preparation of the bulk polymer samples are shown in Table 5. Table 6 shows comparative results for properties of the material produced by this catalyst system and those of equivalent commercial materials. These include:

(a) Physical properties.

(b) Metal content analyses.

(c) Infra-red analyses.

Figure 14.

The effect of pressure upon the viscosity number of the polymer.

See Appendix___Table I for results and polymerization conditions.

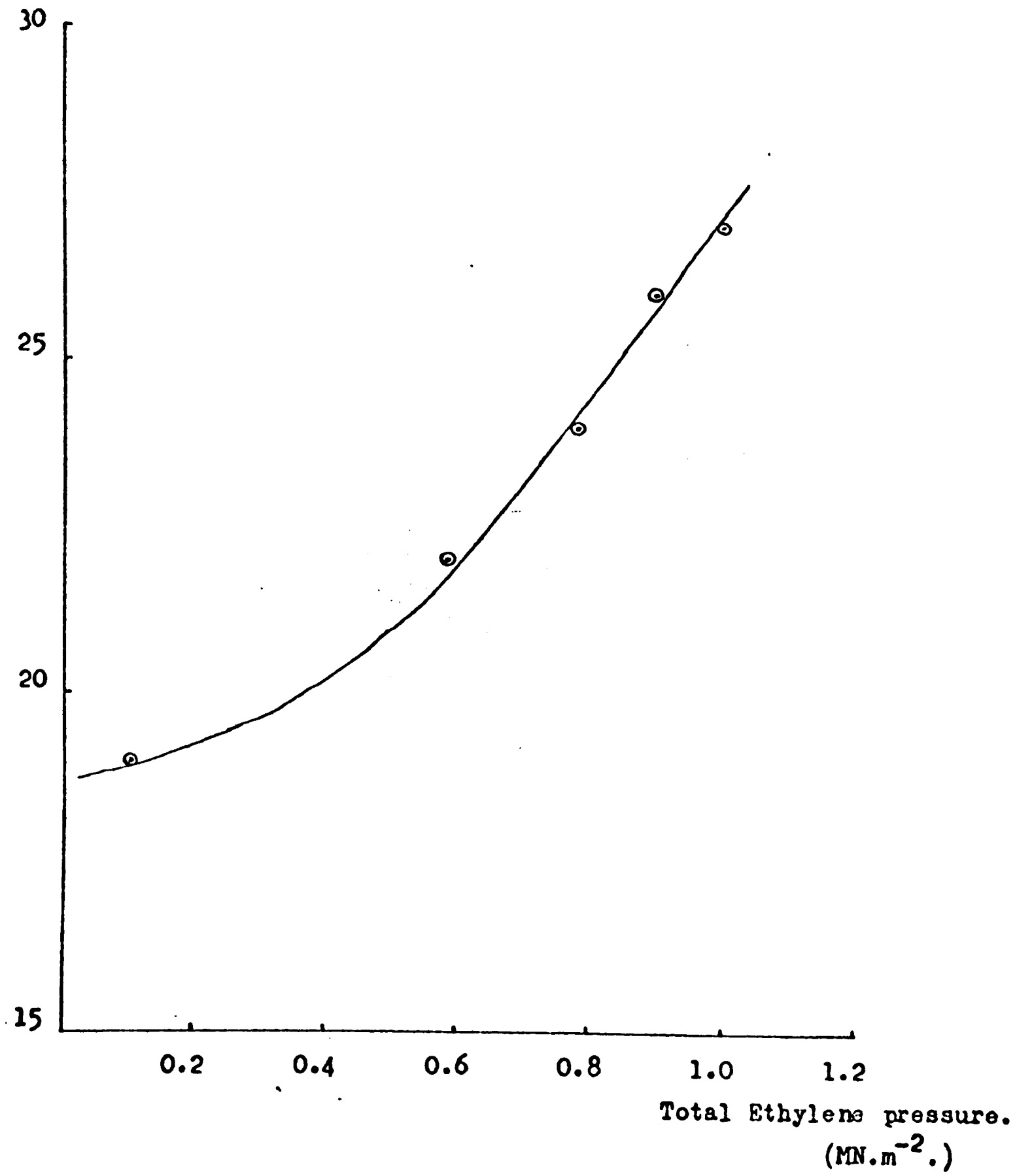


Table 6

Comparative properties of the ultra high molecular weight polymer produced by this catalyst and current commercial materials

a) Physical properties

Sample	Birmingham polyethylene material	Hostalen GUR
Property		
Viscosity number (0.02% solution in dekalin at 135°C) $cm^3gm^{-1} \times 10^{-2}$	25	17
Bulk density $gm.cm^{-3}$	0.25	0.40
Density of homogeneously moulded material, $gm.cm^{-3}$	0.94	0.94

b) Metal content analyses

Sample	Metal content		
	Ti	Al	Cl
	all in parts per million		
Hostalen GUR	9	12	30
Hifax	155	17	55
Birmingham polyethylene material	<1	28	25

I am indebted to Shell Chemicals Ltd. for the results of the elemental analysis of the three materials given above.

CONTD....

Table 6 (Contd.)

c) Infra-red analyses

Sample	Unsaturation (Groups/1000 C atoms)			Total methyl groups / 1000 C atoms Assuming branch lengths greater than C_3 7.25μ *
	Vinyl $-CH=CH_2$ 11.0μ	Trans Vinylene $CH=CH$ 10.34	Vinylidene $C=CH_2$ 11.25	
Hostalen GUR	0.12	0.01 absorption peak just detectable	0.02** absorption peak just detectable	0.5
Hifax 1900	0.02	<0.01 no peak detected	0.02 no peak detected	1 ± 0.2
Birmingham polyethylene	0.04	<0.01 no peak detected	0.02 no peak detected	0.5

* Determination made using a compensating wedge having a total methyl content similar to that of Hifax 1900. Hence Hostalen and Birmingham sample results obtained by extrapolation to an assumed zero and are therefore only approximate at these low levels.

** It is assumed that there is no interference from methyl groups belonging to alkyl chains longer than $-CH_3$.

NOTE: The Birmingham PE sample contains traces of a silicone oil absorption present at 7.9, 9-10 and 12.4 microns).

I am indebted to Mr. G. T. Chamberlain of Shell Research Ltd., Carrington, Manchester for the results given in the Table above.

Section II - The kinetic features of the reaction

When suitable conditions had been established for the preparation of bulk samples of ultra-high molecular weight material, an investigation was undertaken of the principal kinetic features of ethylene polymerization using this catalyst system. The kinetics of the polymerization were studied at atmospheric pressure in the apparatus described earlier (see Figures 10 and 11). The organo-magnesium reduced titanium (III) chloride/aluminium triethyl was used under conditions in which it was shown that the reaction is independent of mass transfer rate. In kinetic investigations of ethylene polymerization it is necessary to pay attention to differentiating clearly between conditions leading to "chemical control" of the reaction and those which result in a mass transfer limited control. The comparatively low solubility of ethylene in hydrocarbons such as iso-octane, coupled with the high reactivity of the catalyst system, can easily lead to polymerizations which are controlled by the rates of gas transfer to the catalyst surface, rather than by chemical factors. Such considerations have been taken into account in the determination of the kinetic rate constant of the polymerization.

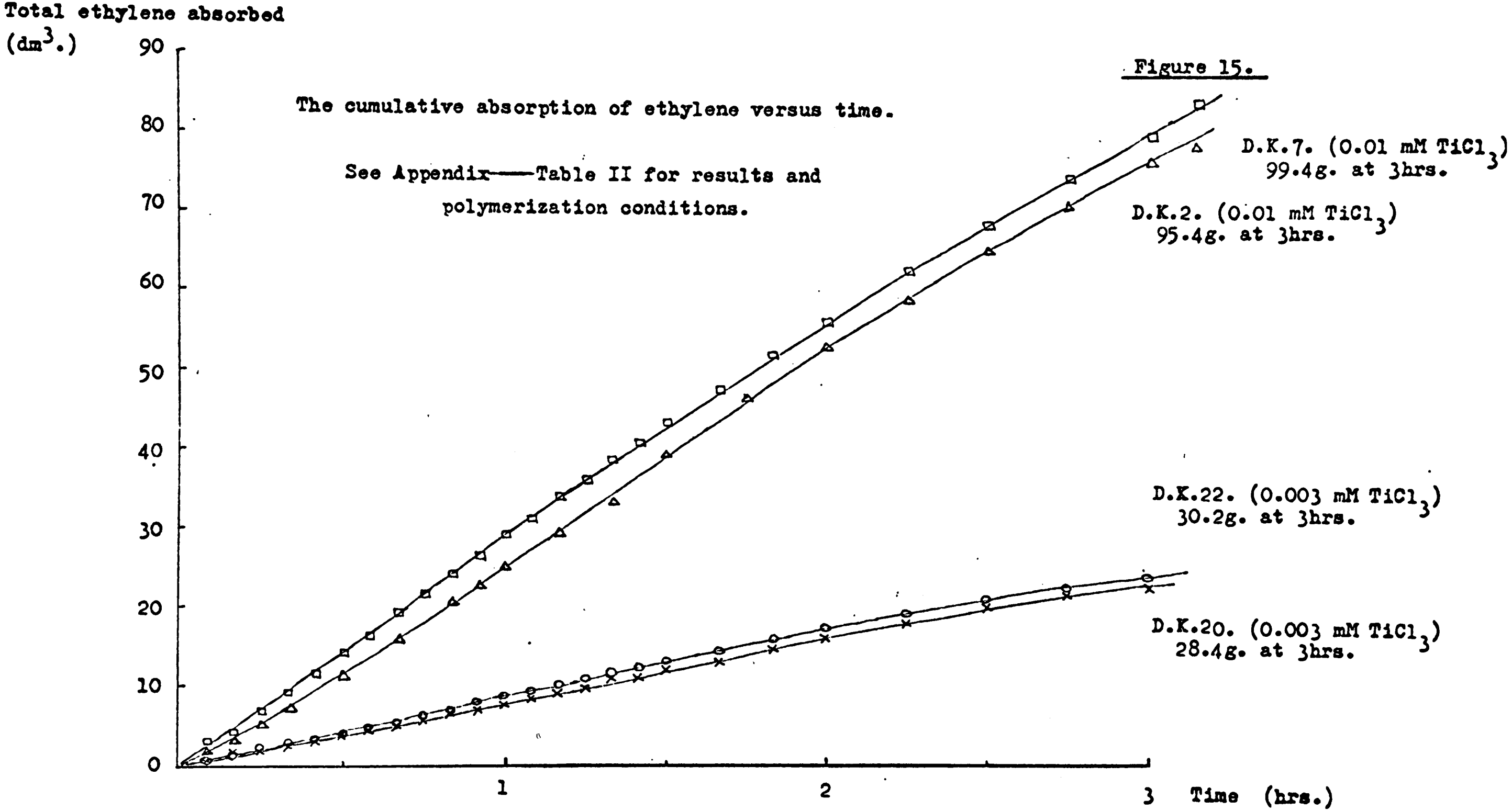
i) General characteristics

The results found for the absorption of ethylene using catalyst concentrations of 0.01 millimolar and 0.003 millimolar titanium (III) chloride are shown in Figure 15 for two runs at each concentration under similar conditions.

Figure 15.

The cumulative absorption of ethylene versus time.

See Appendix——Table II for results and polymerization conditions.



The results illustrate that the reproducibility of the reaction parameters is better at these relatively low conversions than at the high conversions employed in the earlier work where mass transfer limitations have an important effect. In these kinetic experiments it was normally found that the ethylene absorbed in individual experiments was duplicated $\pm \leqslant 10\%$ for polymerizations carried out under identical conditions. Figure 16 shows the typical ethylene absorption rate curves for ethylene polymerizations at catalyst concentrations of 0.01 millimolar and 0.003 millimolar, titanium (III) chloride. The curves show marked changes in absorption rate with time particularly at the higher titanium concentration similar to what is found in certain other Ziegler systems, e.g. "active" titanium III chloride catalysts such as fresh α-,γ-,δ-$TiCl_3$ or AA, HA grade $TiCl_3$ activated by aluminium triethyl[43, 44, 50].

The curves consist of three major parts, as outlined for the decay type kinetics shown in Figure 17. The initial build up period (I) is of relatively short duration and is where the rate builds up to a maximum. The decay period (II) which follows the maximum is the region where the rate gradually declines, and for many of the kinetic experiments in the present work this completes the three hour time scale. However, if longer time scales or certain results at lower activity levels (i.e. lower temperature results) are considered a third region is found where the decreasing rate levels off towards an assymptotic value. This final

Figure 16.

The rate of absorption of ethylene versus time for two concentrations of $TiCl_3$.

See Appendix——Table III for results and polymerization conditions.

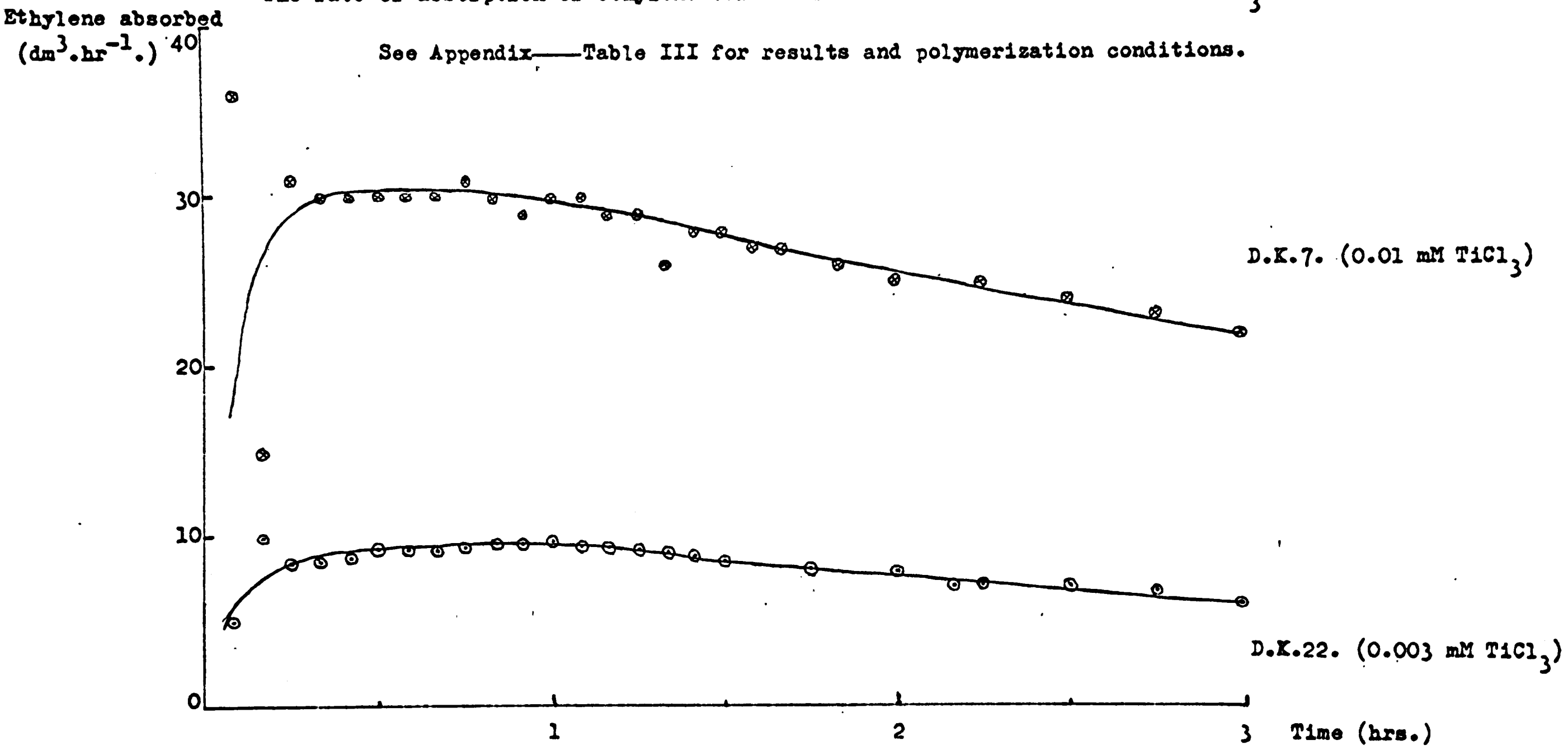
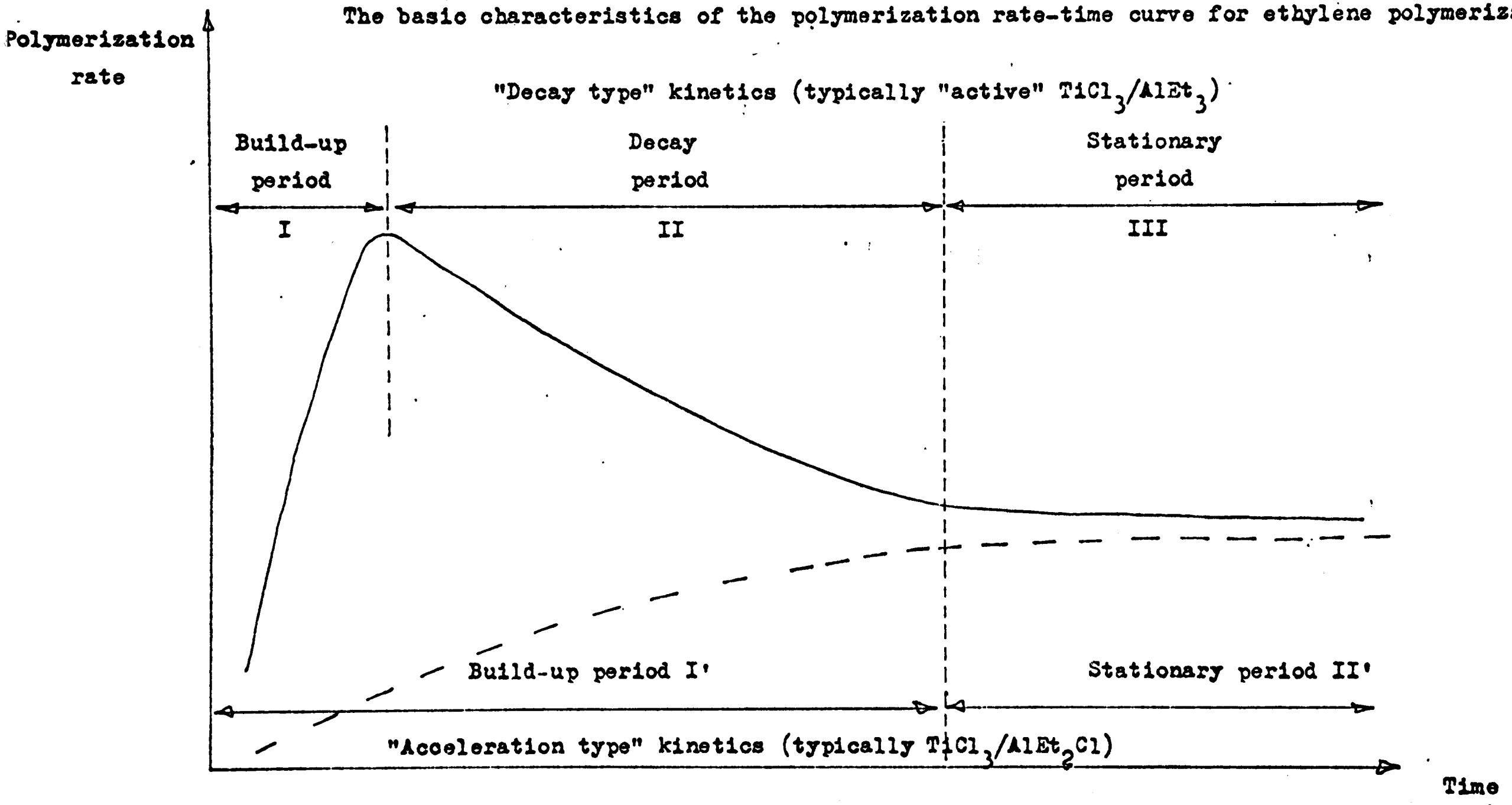


Figure 17.

The basic characteristics of the polymerization rate-time curve for ethylene polymerization.



region (III) is generally[43] known as the stationary period and polymerization can continue steadily at this markedly reduced rate for long periods.

A closer look at the components of the rate time curve shows that the build-up region can be attributed to two causes, the first being an induction period, the time in which the system reaches a balanced condition, i.e. for reaction to take place between the catalyst components and for them to react with the monomer to begin the initiation of the polymer chains. Practical observations show that this induction period must be short as stable rate conditions have generally been attained within the first 5 - 10 minutes of the polymerization. It is at this point where in many cases the other part of the build up may be observed. This is the gradual build up of rate to a maximum which may take from a few minutes (with an active polymerization) to a matter of hours with one at the other end of the scale. This may be attributed, as has been found[44] in other Ziegler systems, to changes in the particle size of the solid catalyst component. In this system changes of the size of the catalyst/growing polymer particles are visible to the naked eye. Although these are large scale phenomena, probably not directly affecting the rate, they can be seen to take place as the absorption rate climbs to its maximum.

Evidence that such changes may occur has been cited by Natta et al[44] who obtained "acceleration type" kinetic curves (lower dotted line in Figure 17) with an unground γ-$TiCl_3$ catalyst component which, however, gave "decay

type" curves when equal samples were used after having been freshly ground. In both cases the rate finally achieved in the stationary period was the same.

In the present work all rate curves were found to follow a decay type pattern. The rate of fall off in the polymerization rate during the decay period was found to vary with the concentration of aluminium alkyl present and at high aluminium concentrations a very marked fall-off in rate was found (Figure 18b).

ii) The effect of aluminium triethyl

The first parameter of the reaction system to be investigated was the concentration of aluminium triethyl and its effect upon the polymerization rate. There is evidence that ethylene can be polymerized slowly on titanium (III) chloride catalyst in the absence of an added alkyl[45, 46], but for a fast reaction it is usually essential to add a minimum concentration of a metal alkyl.

The results obtained by variation of the aluminium concentration in the catalyst system are shown by Figures 18 and 19. Figure 18 a) and b) show the ethylene absorption rate versus time curves for three experiments with aluminium triethyl concentrations from 0.05 - 5.0 millimolar. It can be seen in these results that the decay period in the curve becomes more sharply defined as the concentration of aluminium triethyl employed increases. The following graphs shown in Figure 19 illustrate the aluminium triethyl dependence of the maximum rate of polymerization. This appears to be independent of the

Figure 18a.

The rate of absorption of ethylene versus time for different concentrations of $AlEt_3$.

See Appendix——Table IV for results and polymerization conditions.

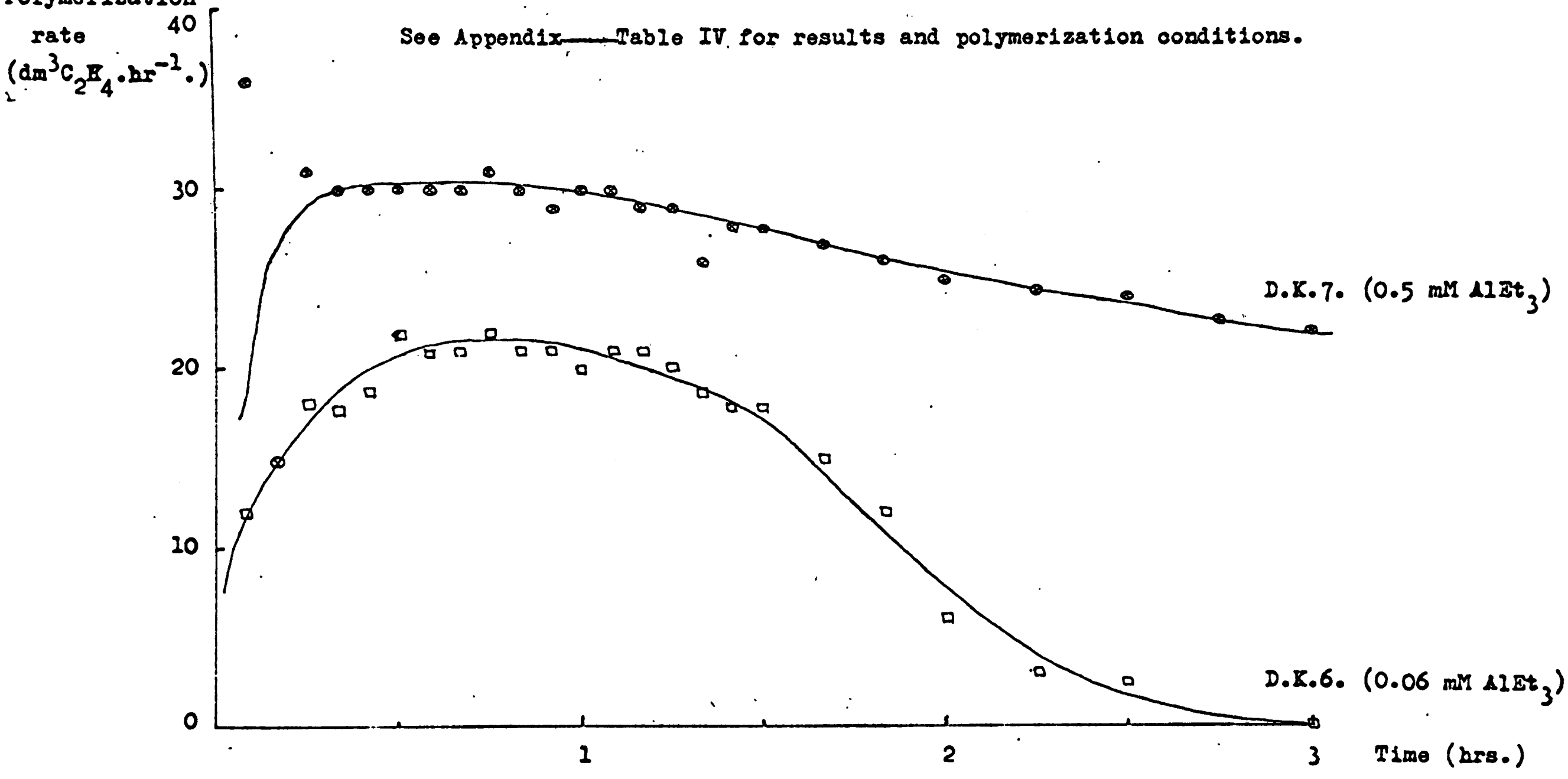


Figure 18b.

The rate of absorption of ethylene versus time for different concentrations of $AlEt_3$.

See Appendix——Table IV for results and polymerization conditions.

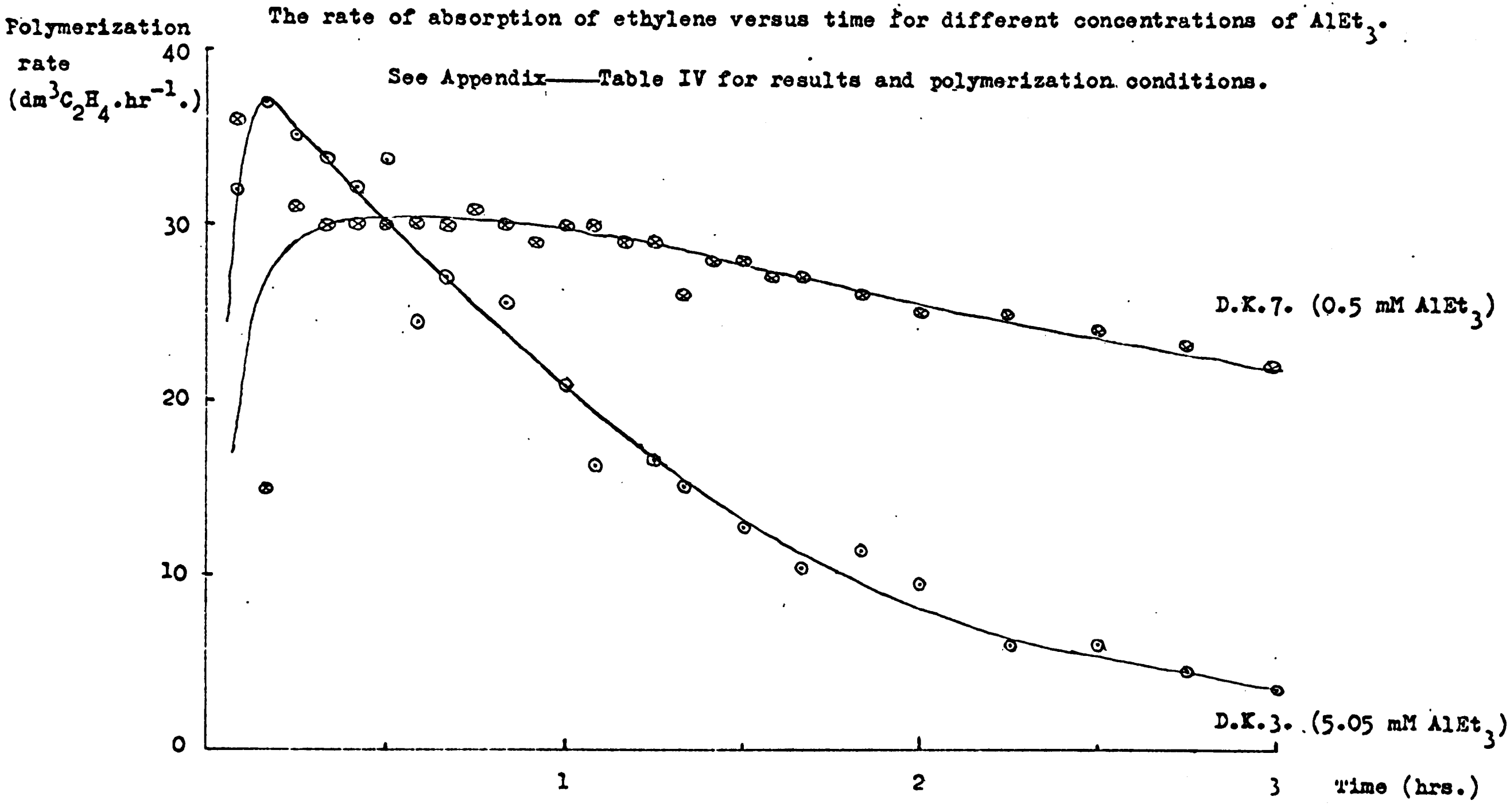
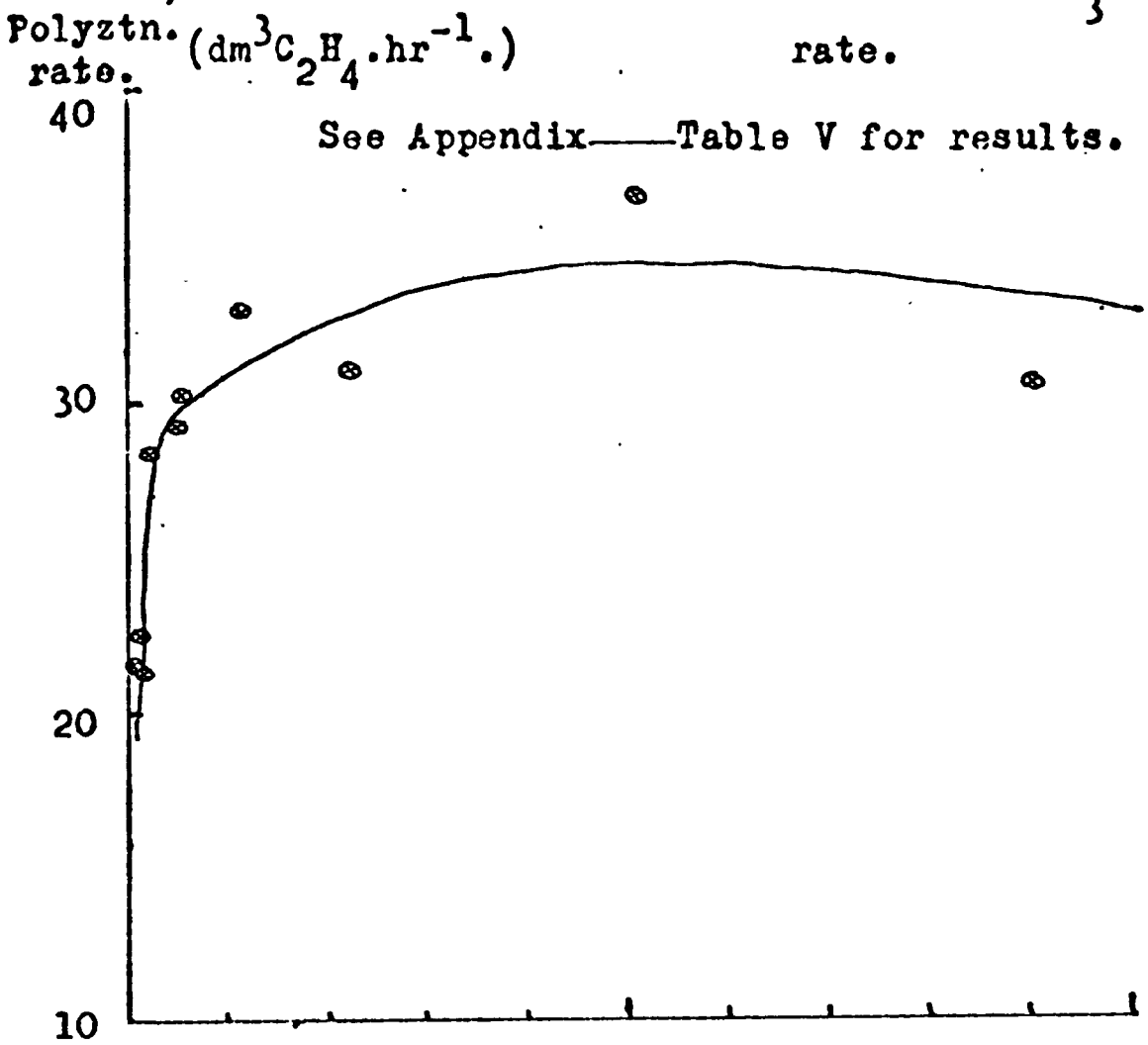
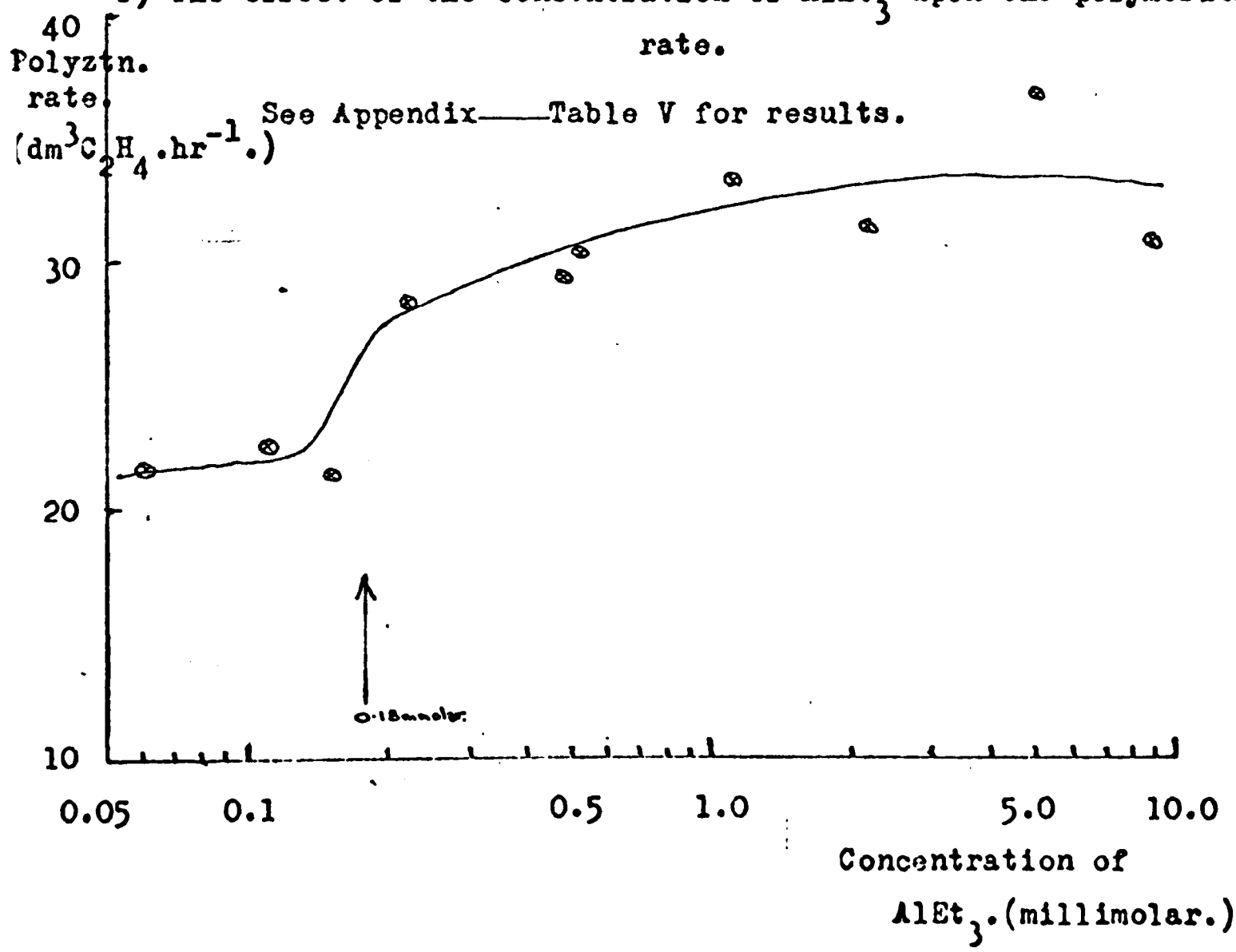


Figure 19.

a) The effect of the concentration of $AlEt_3$ upon the polymerization rate.



b) The effect of the concentration of $AlEt_3$ upon the polymerization rate.



aluminium triethyl concentration for concentrations greater than approximately 0.18 millimolar. This is shown by the sharp rise found in the rate between experiments at concentration about 0.10 mM and those with concentrations >0.20 mM. The linear plot, Figure 19a, best illustrates this marked rise and the fairly level region which follows. Similar observations were also found by Berger and Grieveson using a γ-$TiCl_3/AlEt_2Cl$ system[41].

The rate dependence curve is also illustrated as a logarithmic scale plot, Figure 19b, which shows the region of low activity at low concentrations followed by the sharp rise to the broad maximum which appears to gradually tail off at high concentrations of aluminium triethyl. This behaviour can be attributed to three causes. The results at low aluminium concentrations probably arise due to the dual role of the aluminium alkyl which will act as a scavenger for reactive impurities and thus a certain quantity will be consumed for this reason. This is often the cause of scattered results obtained at very low aluminium triethyl concentrations. The main role of the alkyl, however, is considered to be the production of active sites by alkylation[46] at the surface of the titanium (III) chloride as is thought to take place in other Ziegler systems for ethylene polymerization based on titanium (III) chloride. The remaining alkyl will be used up for this purpose and so the rapid rise in the rate of polymerization, in this particular case at an Al/Ti ratio of about 20, is apparently

due to increasing alkyl being available for this alkylation which, when complete, results in the level part of the curve. The gradual decline which may be detected in the latter part of the curve can be explained by an increasing importance of decay processes at higher aluminium triethyl concentrations (see Figure 18b). This is attributed to termination or transfer processes involving (in this case) triethyl aluminium, although there are other possible mechanisms.

Alternative proposals for decay in $AlEt_3/TiCl_3$ systems are loss of activity due to aluminium triethyl reduction of the titanium.

$$AlR_3 + TiCl_3 \longrightarrow AlR_2Cl + TiCl_2 + R\cdot$$

as cited by Berger and Grieveson[41]. Further alkylation (leading to reduction) of the titanium (III) chloride which in effect amounts to a net removal of surface chlorine atoms has been proposed by Ingberman et al[47]. This removal of chlorine atoms from the $TiCl_3$ leaves a catalyst of changed composition and little activity[48]. However, if this process occurs to a marked extent it results in visible darkening of the solid material. The possibility of encapsulation of the catalyst by polymer, a process used to explain declining rates in propylene polymerizations, has also been considered. However, similar declining rates are found for ethylene polymerization and by both heterogeneous and homogeneous systems (such as the soluble vanadium di(isopropyl salicylate) - aluminium diethyl chloride system) as cited by Berger et al[49], pointing to

a common alternative decay process rather than to encapsulation.

iii) The effect of titanium (III) chloride

The second parameter investigated was the effect upon the polymerization rate of the concentration of titanium (III) chloride. An aluminium triethyl concentration of 0.50 millimoles dm^{-3} was used throughout these experiments. As shown in Figure 19a this concentration appears in the fairly level part of the rate-concentration curve above the threshold (0.20 millimolar) concentration. Rate versus time curves for two titanium concentrations are given in Figure 16 and show that there is an increase in rate with increasing titanium concentration.

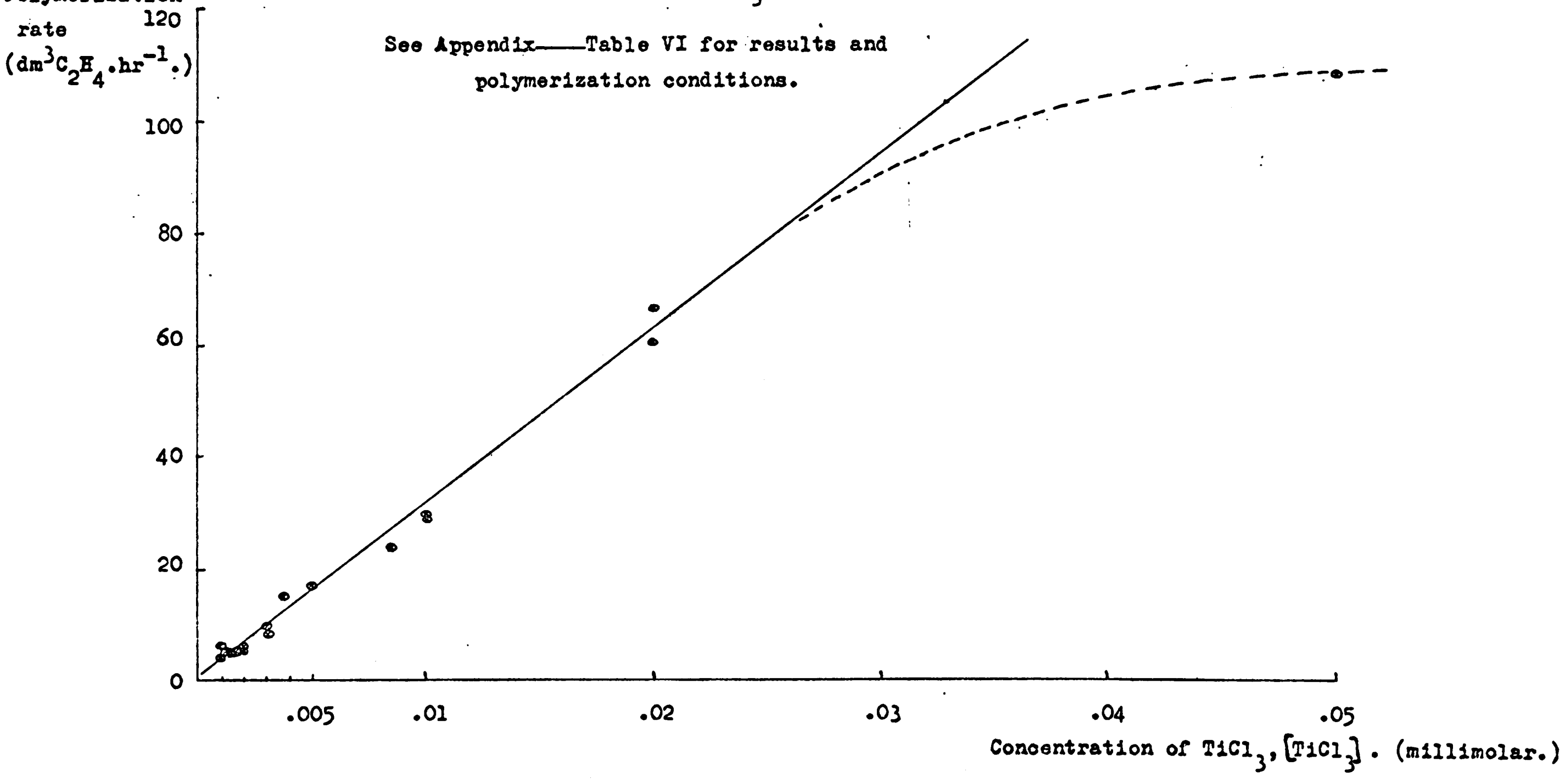
The simplest model of Ziegler catalyst systems assumes that the insoluble titanium (III) chloride particles have active polymerization sites on their surface. Such a model predicts that the rate of polymerization is proportional to the amount of titanium (III) chloride surface present. As shown by Figure 20 this relationship is upheld for the present case, assuming that the Ti/surface ratio is constant, over the range of concentrations from 0.001 - 0.02 millimolar, but for concentrations >0.02 is found to deviate. The linear relationship is only upheld providing there are no mass transfer effects of the type mentioned previously and as can be seen in the graph these were generally encountered for catalyst concentration >0.02 millimolar in titanium for polymerizations at $50^{o}C$.

In a heterogeneous catalyst system as used for the

Figure 20.

The effect of the concentration of $TiCl_3$ upon the polymerization rate.

See Appendix——Table VI for results and polymerization conditions.



present work it should be noted that the catalyst concentration may not be the only parameter concerned with catalyst activity. The nature of the crystalline surface and the structure of the crystal influence the polymerization rate and also the structure of the polymer (when used for stereoregular polymerization of substituted monomers). These properties of the crystals are dependent upon the technique used to prepare the titanium (III) chloride. For this reason care was taken to ensure the conditions outlined in the procedure for catalyst preparation could be exactly replicated in order to avoid variation in catalyst activity between different samples.

In the case of organo-aluminium reduced catalysts it is generally considered that appreciable quantities of aluminium chloride produced during reduction may be present in the crystal lattice. The organo-magnesium reduced catalysts are similarly considered to incorporate magnesium reduction products into the titanium (III) chloride lattice and it is to this that the much greater activity of the present system is attributed, at least partly because this incorporation of magnesium utterly disrupts the $TiCl_3$ crystal lattice[50].

As shown in Figure 20, for the present catalyst system, the polymerization rate is directly proportional to the concentration of the titanium present. This apparently confirms that the rate of polymerization is governed by chemical factors, and that the rate of transport of monomer is not exceeded by the rate of

reaction, so that the transport rate becomes the rate limiting process. In instances where mass transport is rate limiting,the response of the polymerization rate to the catalyst concentration will be reduced at the higher values and the direct relationship breaks down. In order to ensure that useful measurements could be made before such conditions occurred,it was found desirable to adopt an efficient method for dissolving the monomer gas into the liquid diluent and to employ good agitation in order to eliminate monomer concentration gradients within the diluent. For this purpose the dip tube and stirrer patterns shown in the diagrams of Figure 11 and 13 were used at a stirring rate of 600 r.p.m. during polymerizations. The use of relatively low temperatures and reaction rates also helped to maintain an effective equilibrium between the gas phase and the diluent.

In order to eliminate the problem of interference in the determination of the kinetic rate by mass transport limitations,the following concept applied by Boocock and Haward to a similar Ziegler system was employed.[40] The polymerization is considered to involve the following series of processes for ethylene consumption, all of which must run at the same rate and in this sense be in equilibrium with each other:

(1) The dissolution of monomer gas into the solvent across a gas/liquid interface.

(2) The diffusion of the dissolved monomer to the catalyst surface through the diluent film surrounding the catalyst particles.

(3) The polymerization of the adsorbed monomer layer on the catalyst particle.

By consideration of these processes the following expression can be derived:

If - C_o = Saturation concentration of monomer in the diluent at the polymerization temperature.

C = Actual concentration of monomer in diluent during polymerization.

C_s = Concentration of monomer in diluent which would be in equilibrium with the actual surface concentration of ethylene on the $TiCl_3$.

[Ti] = Concentration of active $TiCl_3$.

then the following expressions can be written:

Rate of solution of ethylene: = K_1 X $(C_o - C)$.....(1)

K represents liquid/gas transfer coefficient

X represents liquid/gas interfacial area dependent upon agitation

Rate of film diffusion at particle/liquid interface: = K_2 [Ti] $(C - C_s)$.....(2)

Rate of polymerization: =R=K_3 [Ti] C_s.....(3)

by combination of (2) and (3),

$$C_s = \frac{K_2 C}{(K_2 + K_3)}$$

by combination of (1) and (3),

$$C = \frac{K_1 X C_o}{K_1 X + \frac{K_3 [Ti] K_2}{(K_2 + K_3)}}$$

now, $R = K_3 [Ti] C_s$

$$= K_3 [Ti] \frac{K_2 C}{(K_2 + K_3)}$$

$$= \frac{K_3 [Ti] K_2}{K_2 + K_3} \left[\frac{K_1 X C_o}{K_1 X + \frac{K_3 [Ti] K_2}{K_2 + K_3}} \right]$$

$$= \frac{K_1 K_2 K_3 X [Ti] C_o}{K_1 X (K_2 + K_3) + K_2 K_3 [Ti]}$$

This relationship indicates a linear correlation between $1/R$ and $1/[Ti]$, since if the film diffusion effect is neglected then:

$$C = C_s, \text{ i.e. } K_2 \gg K_3$$

Then $K_2 + K_3 \longrightarrow K_2$

and $$\frac{1}{R} = \frac{1}{K_3 [Ti] C_o} + \frac{1}{K_1 X C_o} \quad \text{.....(4)}$$

This relationship provides for the overall polymerization rate in terms of the kinetic rate function and mass transport function. It also extends to include a diffusion film of polymer around the catalyst particle when applicable, providing it can be assumed that this remains constant with time.

The application of equation (4) to the experimental

results in the present work gives the results shown in Figure 21, which is a plot of the reciprocal of the maximum polymerization rate versus the reciprocal of the titanium catalyst concentration. This is found to give a linear plot in which the slope is controlled by the catalytic activity. The intercept gives the maximum rate at which, under the given experimental conditions, ethylene can be transferred into the solvent. The results obtained show a fairly wide margin of scatter for values of $1/[Ti]$ greater than 750, as in this region they approach the practical limits of ethylene absorption measurement for the present apparatus, i.e. 0.001 millimolar Ti concentration and 4 - 5 $dm^3 hr.^{-1}$ ethylene consumption. The values derived from the data are:-

Maximum transfer rate = 330 $dm^3 C_2H_4$ $hr.^{-1}$

Maximum rate of polymerization

= 3356 dm^3 Ethylene at STP (millimoles $TiCl_3.dm^{-3}$ solvent)$^{-1}$ $hr.^{-1}$ atmosphere^{-1}

= 971.7 moles Ethylene.(gm $TiCl_3$)$^{-1}$ $hr.^{-1}$ atmosphere^{-1}

= 27,200 gm. Ethylene (gm $TiCl_3$)$^{-1}$ $hr.^{-1}$ atmosphere^{-1}

Maximum rate constant , K_3 *

= 8057 moles Ethylene (molar Ethylene conc. in saturated solution)$^{-1}$ (gm $TiCl_3$)$^{-1}$ $hr.^{-1}$ atmosphere^{-1}

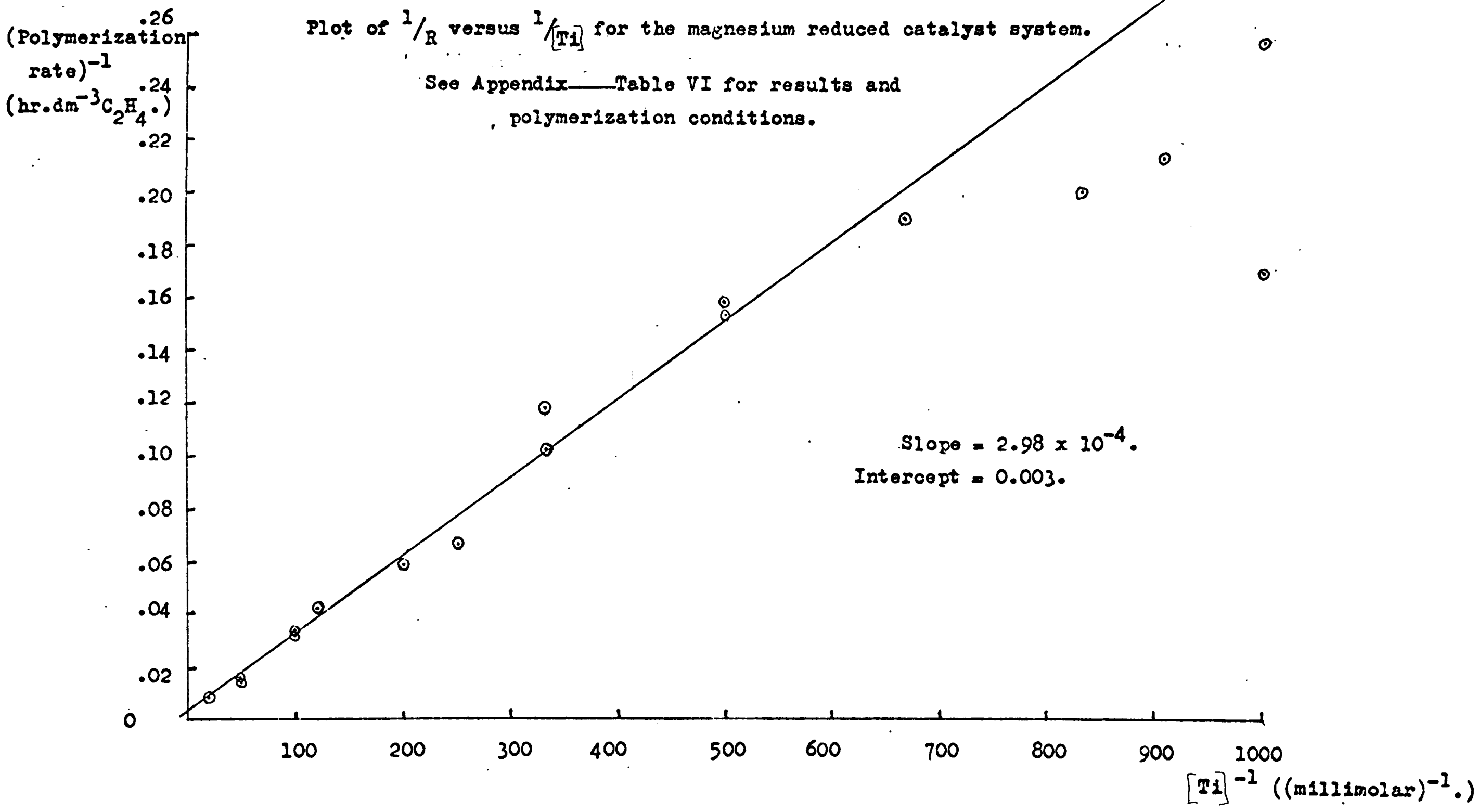
8057 gm. Ethylene (gms Ethylene dissolved in saturated solution)$^{-1}$ (gm $TiCl_3$)$^{-1}$ $hr.^{-1}$ atmosphere^{-1}

* (see Appendix Note 1)

Figure 21.

Plot of $^{1}/_{R}$ versus $^{1}/_{[Ti]}$ for the magnesium reduced catalyst system.

See Appendix——Table VI for results and polymerization conditions.



Note: [1 atmosphere = 1 x 10^5 Nm^{-2}]

(iv) The effect of temperature

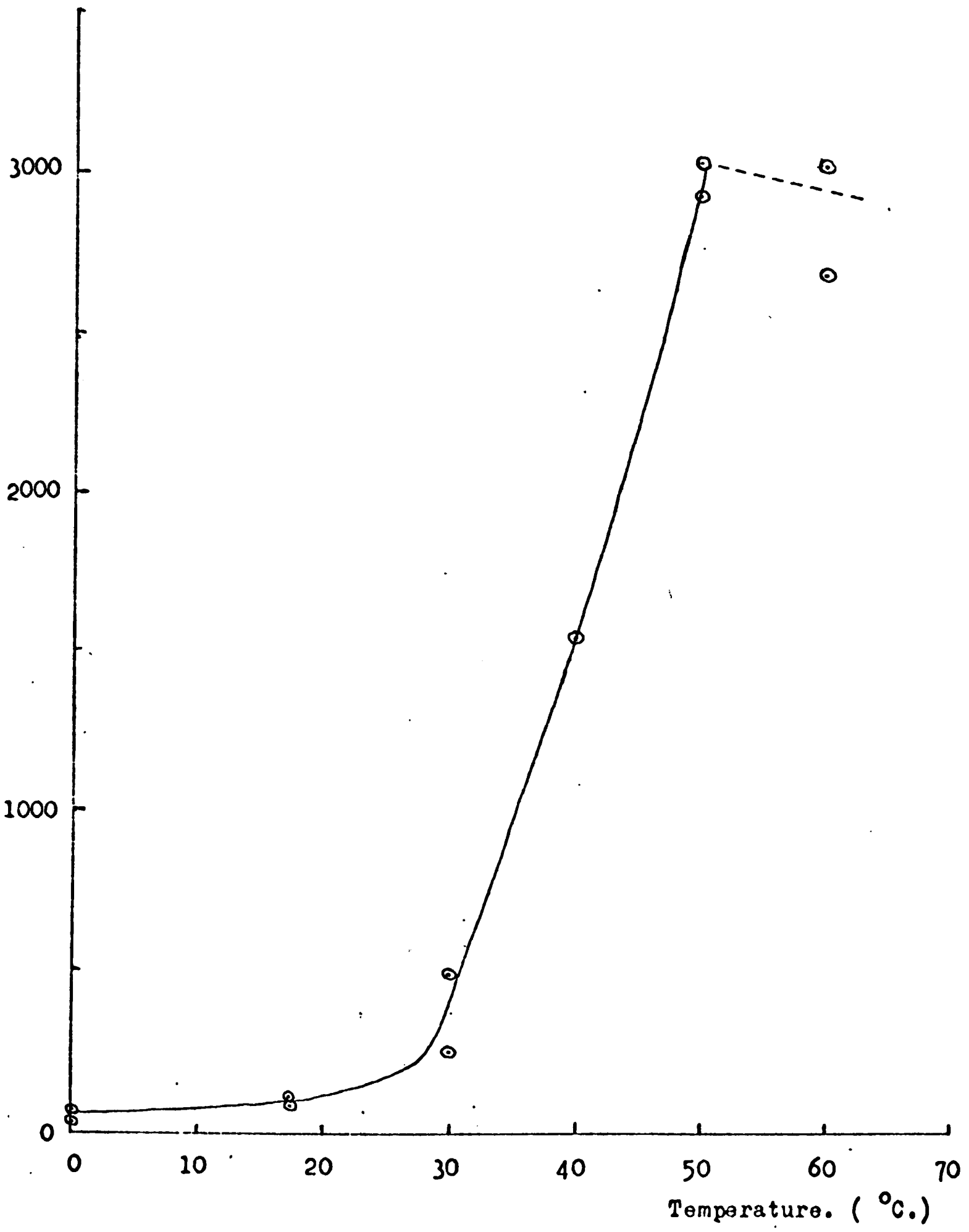
Figure 22 shows the effect of different polymerization temperatures upon the maximum polymerization rate. The rate is found to increase with temperature up to approximately 50°C. The curve is rather slow to rise from 0°C. to just over 20°C. but then climbs very sharply to 50°C. Beyond 50°C. it appears to flatten off and results obtained at 60°C. show no further increase in rate but suggest that the rate may be beginning to decline. This discontinuity in the increase of rate with temperature has been found in other investigations of Ziegler systems: Berger and Grieveson[41] found a similar result for ethylene polymerization using a γ- $TiCl_3/AlEt_2Cl$ catalyst system at temperatures 50°C. They attributed this to a diminution in the rate of solution of ethylene arguing that at temperatures 50°C., this is too low to satisfy the potential polymerization activity of the catalyst at the concentrations they employed.

However, there is alternatively the possibility that at high temperatures there may be some destruction of the active polymerization sites, particularly in the present case where aluminium triethyl may be involved (see earlier comments on the possible role of $AlEt_3$ in the decay period). At these higher temperatures the catalyst system may become less active due to reduction of the $TiCl_3$ by the aluminium triethyl to give inactive species[41, 47, 48]. A similar reaction between aluminium tri-isobutyl and vanadium trichloride has been used to explain a similar effect in

Figure 22.

The effect of temperature upon the polymerization rate.

See Appendix——Table VII for results.



the polymerization of 4-methylpentene-1 by McKenzie, Tait and Burfield[51].

Figure 23 shows an Arrhenius plot of these results for rate and temperature. This confirms a linear relationship between the temperatures of 0°C. and 50°C. from which the overall apparent activation energy of 75.8 kJ $mole^{-1}$ (18.1 Kcal $mole^{-1}$) for the polymerization reaction has been determined. This value is rather higher than those which have been obtained for ethylene with other Ziegler systems[52], albeit it compared favourably with the value of 72.4 kJ $moles^{-1}$ (17.3 Kcal $mole^{-1}$) found by Berger and Grieveson[41] for the γ-$TiCl_3/AlEt_2Cl$ system at constant monomer concentration. Most authors however reported values from 4.2 to 50.2 kJ $mole^{-1}$ (1 to 12 Kcal $mole^{-1}$) and Fukui[53] obtained an activation energy of 32.6 kJ $mole^{-1}$ (7.8 Kcal $mole^{-1}$) at constant monomer concentration for a $TiCl_3/Al(C_2H_5)_3$ system, a value substantially lower than that found in the present work. However, some discrepancies might be expected with the overall activation energy term estimated here, as it is a compound value which includes contributions from sources other than the activation energy of the polymerization reaction; one obvious complication is the temperature variation of thesolubility of ethylene in the diluent.

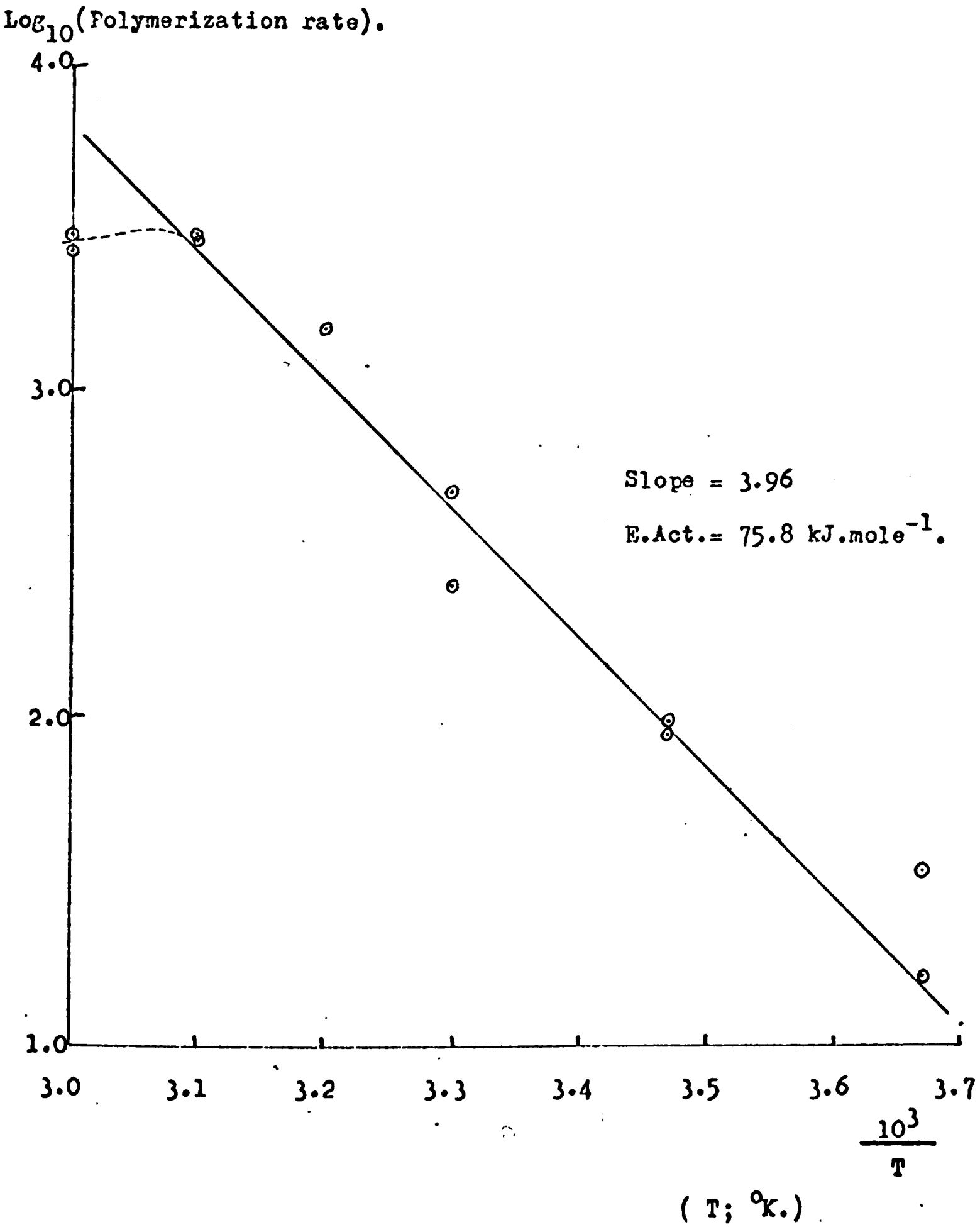
Section III - An investigation of the molecular weight behaviour of the reaction

The previous section outlined the main kinetic features of the organo-magnesium reduced titanium (III) chloride

Figure 23.

An Arrhenius plot of polymerization rates obtained using the magnesium reduced $TiCl_3$ catalyst system.

See Appendix——Table VII for results.



catalyst system used in the present work. In this chapter the influence of the polymerization conditions, i.e. catalyst composition and reaction temperature, upon the molecular weight of the polymer produced are discussed. Results from the study of the change in molecular weight with time are also presented. These are used together with overall polymerization rate data to provide estimates of the concentration of active catalytic sites and the lifetime of the growing polymer chain.

(i) General considerations

Estimation of the limiting viscosity number

The molecular weight of the polymer samples was estimated by viscometry. The limiting viscosity number was determined by the application of a one-point method devised by Elliott, Horowitz and Hoodock[54] for a single determination carried out by the standard techniques using, in the present case, a 0.02% w/v solution in dekalin at 135°C.

The results obtained from this method correlated well with those obtained by the experimental determination of the limiting viscosity number (L.V.N.) by extrapolation to zero concentration of the viscosity number for a series of solutions. The agreement is illustrated by the results in Table 7, which shows values for the L.V.N. calculated by the one-point method and results obtained by extrapolating experimental measurements using plots of $\frac{t - t_o}{t_{oc}}$ and

$\text{Log}_e \frac{t/t_o}{c}$ versus concentration.

The one-point method is based upon the Martin equation:

$$\text{Log}\ (\eta_{sp}/c) = \text{Log}[\eta] + k[\eta]c$$

where $[\eta]$ has units $cm^3 gm^{-1} \times 10^{-2}$

c has units $gm.cm^{-3} \times 10^{-2}$ (see Appendix Note 2)

which Elliott et al[54] have shown by statistical analysis of viscosity data from a wide range of polyethylene and polypropylene samples to fit experimental data better than the Huggins equation:

$$\eta_{sp}/c = [\eta] + K^1[\eta]^2 c$$

especially at high values of $[\eta]c$ (i.e. particularly with samples having high L.V.N.).

The statistical analysis of the viscosity data gave an average value of K = 0.139 covering both polyethylene and polypropylene samples. By using this value in the Martin equation it can be expressed in the following form:

$$\eta_{rel} = 1 + c[\eta]e^{0.320[\eta]c}$$

From this equation tables were drawn up to permit the calculation of the L.V.N. from a single relative viscosity measurement at 0.02% concentration. No kinetic energy corrections were made in the calculations of the viscosity data as the efflux time of the solvent was long enough, (~100 sec.) to make such corrections negligible for the viscosity numbers involved in this work.

The effect of shear rate upon polyethylene solutions was investigated by Elliott et al[54], who found that it could be described empirically by the following equation:

Table 7

Comparative results for the determination of the limiting viscosity number by the one point method and by the multi-point technique

Sample	Limiting viscosity number ($cm^3gm^{-1} \times 10^{-2}$)							
	Multi-point method			Single point method				
	$\frac{t - t_o}{t_o c}$	$\frac{Log_e t/t_o}{c}$	Multi-point average	% conc. of single point measurement				
				0.50	0.10	0.05	0.02	Single point ave.
B.P. Rigidex	1.26	1.26	1.26	1.31	-	1.27	-	1.29
Shell Carlona	1.37	1.37	1.37	1.35	1.37	1.40	-	1.37
PT.1	6.15	5.95	6.05	-	6.31	6.18	6.08	6.19
PT.2	8.40	8.40	8.40	-	8.49	8.50	8.38	8.46
PT.3	10.1	10.5	10.3	-	12.61	12.16	10.77	11.85
DP.1	21.0	21.4	21.2	-	-	20.81	22.89	21.85
DP.2	23.0	23.0	23.0	-	-	22.50	22.64	22.57
OP.2	12.5	12.9	12.7	-	-	12.43	13.21	12.82
OP.4	31.5	30.5	31.0	-	-	29.90	31.63	30.76

$$\eta_{sp}(\gamma = 0) = \eta_{sp}\left(1 + 1.5 \times 10^{-4}\, \eta_{sp}\, \gamma\right)$$

where $\eta_{sp}(\gamma = 0)$ is the specific viscosity at zero shear rate

η_{sp} is the specific viscosity at the shear rate, γ

Assuming that the experimental data obeys this equation it follows from it that any shear rate correction disappears as η_{sp} (and also the concentration) approaches zero. In using the Martin equation an extrapolation to zero concentration is included which results in the elimination of the necessity for shear rate correction.

Calculation of $\bar{M}_n$

The estimate of the number average molecular weight was obtained from the limiting viscosity number results by using this relationship.

$$[\eta] = 2.3 \times 10^{-4} (\bar{M}_n)^{0.82}$$

The first empirical relationship between molecular weight and L.V.N. was proposed by Staudinger[55],

$$[\eta] = kM$$

where k is a constant of the particular polymer-solvent system.

M is the polymer molecular weight.

but its validity was found to be rather limited. Subsequently, the more widely accepted general empirical relationship known as the Mark-Houwink equation was proposed[56].

$$[\eta] = kM^{\alpha}$$

k, α, are constants for a given polymer, solvent, and temperature

M is the molecular weight of a homogeneous fraction of polymer.

The expression quoted above is of this type and was derived by De la Cuesta and Billmeyer[57] for fractions of linear polyethylene in dekalin at 135°C., where the number average molecular weight can be related to the limiting viscosity number using the constants $k = 2.3 \times 10^{-4}$, $\alpha = 0.82$. In the present case the relationship has been applied to whole polymer samples for the calculation of $\bar{M}_n$.

This number is likely to be only a rather poor estimate of the true $\bar{M}_n$, but as no technique for the direct measurement of $\bar{M}_n$ was available to us, this method was considered to be the best and most convenient estimate obtainable.

Table 8 includes for comparison the values for $\bar{M}_n$ calculated as outlined above from the viscosity data and values obtained by molecular weight distribution analysis using gel permeation chromatography apparatus. The latter results were obtained by the Rubber and Plastics Research Association. The variables employed in the gel permeation chromatography analysis are given in the Appendix, Table XV.

The gel permeation chromatography results show discrepancies from those obtained from the viscometry measurements. However, R.A.P.R.A. experienced difficulty with these very high molecular weight polyethylene samples, in obtaining the filtered solutions required for gel permeation chromatography. It was found that the samples "gelled" very easily below 140°C. and there is the strong possibility that some of the high molecular weight material may have been removed during filtration, or that there may have been degradation due to shear. The results of the g.p.c. analysis do however show that there is relatively little change in the molecular weight distribution with time under identical conditions. A comparison of the results for $\frac{\bar{M}_w}{\bar{M}_n}$ at 5 mins. and at 1 hour for the same experiment (- samples 1 and 2.) show that this remains relatively constant with values of 10.4 and 9.1 respectively. This can be used to

support the assumption that the molecular weight distribution remains constant for the period during which measurements are taken. This is important when comparing the molecular weight derived from viscosity measurements for samples removed at different reaction times, as the $[\eta]$ - M_n relationship also shows a marked dependence upon the molecular weight distribution. Therefore, the latter is assumed to be constant for all the polymer samples.

In the viscosity determinations carried out in the present work it was found progressively more difficult to obtain accurate viscosity measurements as $[\eta]$ increased. Sample solutions with viscosity numbers in the region of $30\ cm^3gm^{-1} \times 10^{-2}$ were very susceptible to gel formation, as was found in the g.p.c. analyses, particularly if allowed to cool below 135°C. at any stage. High viscosity samples were also particularly susceptible to oxidation if the solutions were heated at temperatures greater than 150°C. for more than three hours. The value of $[\eta]$ was calculated as described from an average value of η_{rel} obtained from three separate measurements. The reproducibility between measurement was generally $\pm \geqslant 15\%$ in terms of the relative viscosity.

Figure 24 shows how the molecular weight of the polymer changes with reaction time during the course of a six hour polymerization. There is initially a rapid rise in the molecular weight which takes place during the first 15-20 minutes of the polymerization. This falls off at about 20 minutes and subsequently the molecular weight is found to build up gradually until it appears to approach a

Figure 24.

The change of molecular weight with time.

See Appendix——Table VIII for results.

Polymerization conditions: Atmospheric pressure, 50°C, 0.01 millimolar $TiCl_3$, 0.5 millimolar $AlEt_3$.

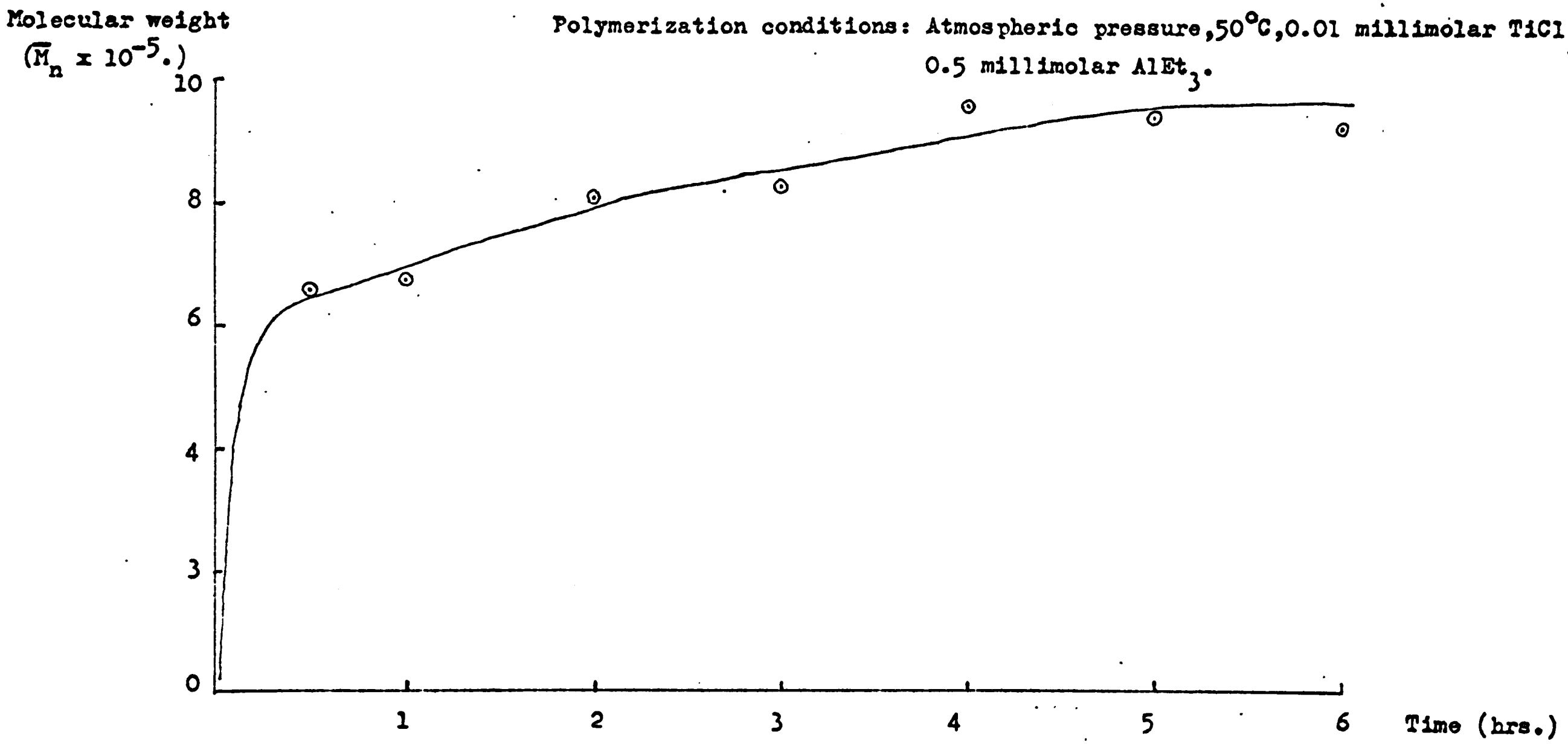


Table 8

Comparative results for the estimation of the number average molecular weight from viscometry measurements and from gel permation chromatography measurements

Sample 1

Polymerization conditions: temperature - 50°C., reaction time - 5 mins., total ethylene pressure - atmospheric, aluminium triethyl concentration - 0.50 millimolar, dodecyl magnesium bromide reduced $TiCl_3$ concentration - 0.01 millimolar.

Gel permeation chromatography results	Viscometry results
$\bar{M}_n = 1.45 \times 10^5$	$\bar{M}_n = 3.40 \times 10^5$
$\bar{M}_w = 1.51 \times 10^6$	$\bar{M}_w = 1.17 \times 10^6$
$\bar{M}_v = 9.31 \times 10^5$	$\bar{M}_v = 6.32 \times 10^5$
$\frac{\bar{M}_w}{\bar{M}_n} = 10.44$	$[\eta] = 7.9\ cm^3 gm^{-1} \times 10^{-2}$

Sample 2

Polymerization conditions: temperature - 50°C. reaction time - 60 mins., all other variables as sample 1.

Gel permeation chromatography results	Viscometry results
$\bar{M}_n = 3.02 \times 10^5$	$\bar{M}_n = 6.77 \times 10^5$
$\bar{M}_w = 2.73 \times 10^6$	$\bar{M}_w = 2.52 \times 10^6$
$\bar{M}_v = 1.69 \times 10^6$	$\bar{M}_v = 1.30 \times 10^6$
$\frac{\bar{M}_w}{\bar{M}_n} = 9.05$	$[\eta] = 13.9\ cm^3 gm^{-1} \times 10^{-2}$

Table 8 (Contd.)

Sample 3

Polymerization conditions: temperature - 50°C., reaction time - 3 hrs., total ethylene pressure - 1.0 MNm^{-2} (10 atmospheres), aluminium triethyl concentration - 0.15 millimolar, octyl magnesium bromide reduced $TiCl_3$ concentration - 0.002 millimolar.

Gel permeation chromatography results	Viscometry results
$\bar{M}_n = 1.46 \times 10^5$	$\bar{M}_n = 1.15 \times 10^6$
$\bar{M}_w = 8.87 \times 10^5$	$\bar{M}_w = 4.53 \times 10^6$
$\bar{M}_v = 4.66 \times 10^5$	$\bar{M}_v = 2.28 \times 10^6$
$\frac{\bar{M}_w}{\bar{M}_v} = 6.07$	$[\eta] = 21.5\ cm^3 gm^{-1} \times 10^{-2}$

Sample 4

Polymerization conditions: As for sample 3 above

Gel permeation chromatography results	Viscometry results
$\bar{M}_n = 2.59 \times 10^5$	$\bar{M}_n = 1.65 \times 10^6$
$\bar{M}_w = 1.93 \times 10^6$	$\bar{M}_w = 6.73 \times 10^6$
$\bar{M}_v = 1.26 \times 10^6$	$\bar{M}_v = 3.32 \times 10^6$
$\frac{\bar{M}_w}{\bar{M}_v} = 7.44$	$[\eta] = 28.8\ cm^3 gm^{-1} \times 10^{-2}$

Notes:

i) Variables used in the g.p.c. work are quoted in the Appendix.

ii) The following relationships were used for calculation of $\bar{M}_w$[57] and $\bar{M}_v$[66] from the limiting viscosity number, $[\eta]$.

Table 8 (Contd.)

De la Cuesta and Billmeyer

$\bar{M}_w$: $= 2.55 \times 10^{-4} (\bar{M}_w)^{0.74}$

Duch and Küchler

$\bar{M}_v$: $= 2.36 \times 10^{-4} (\bar{M}_v)^{0.78}$

---

limiting value during the latter half of the reaction. In the present case under the given conditions this is when $\bar{M}_n \sim 1 \times 10^6$. Similar behaviour has been found in other Ziegler systems[42, 58, 59, 60].

(ii) The effect of aluminium triethyl

The plot shown in Figure 25 shows the relationship of the L.V.N. (and the derived $\bar{M}_n$) to the concentration of aluminium triethyl used. These results were all obtained from three hours polymerizations at a constant titanium concentration of 0.01 millimolar. The plot shows that as the concentration of the aluminium triethyl increases the molecular weight of the polymer decreases. This agrees with reports from several authors using MCl_3/AlR_3 catalyst systems[60, 61, 62]. It is generally interpreted as arising from chain transfer with aluminium alkyl. This has been demonstrated to occur with adsorbed alkyl in the polymerization of 4-methyl pentene-1 using a $VCl_3/Al(isobutyl)_3$ system by Burfield, Tait and McKenzie[63, 64]. However, this finding does not agree with that of Grieveson[58] who reports constant values of $[\eta]$ for variation in aluminium diethyl chloride concentration from 2.6 to 52 millimolar in the polymerization of ethylene by the γ-$TiCl_3/AlEt_2Cl$ system.

Figure 25a.

The effect of the concentration of $AlEt_3$ on the limiting viscosity number of the polymer.

See Appendix——Table IX for results.

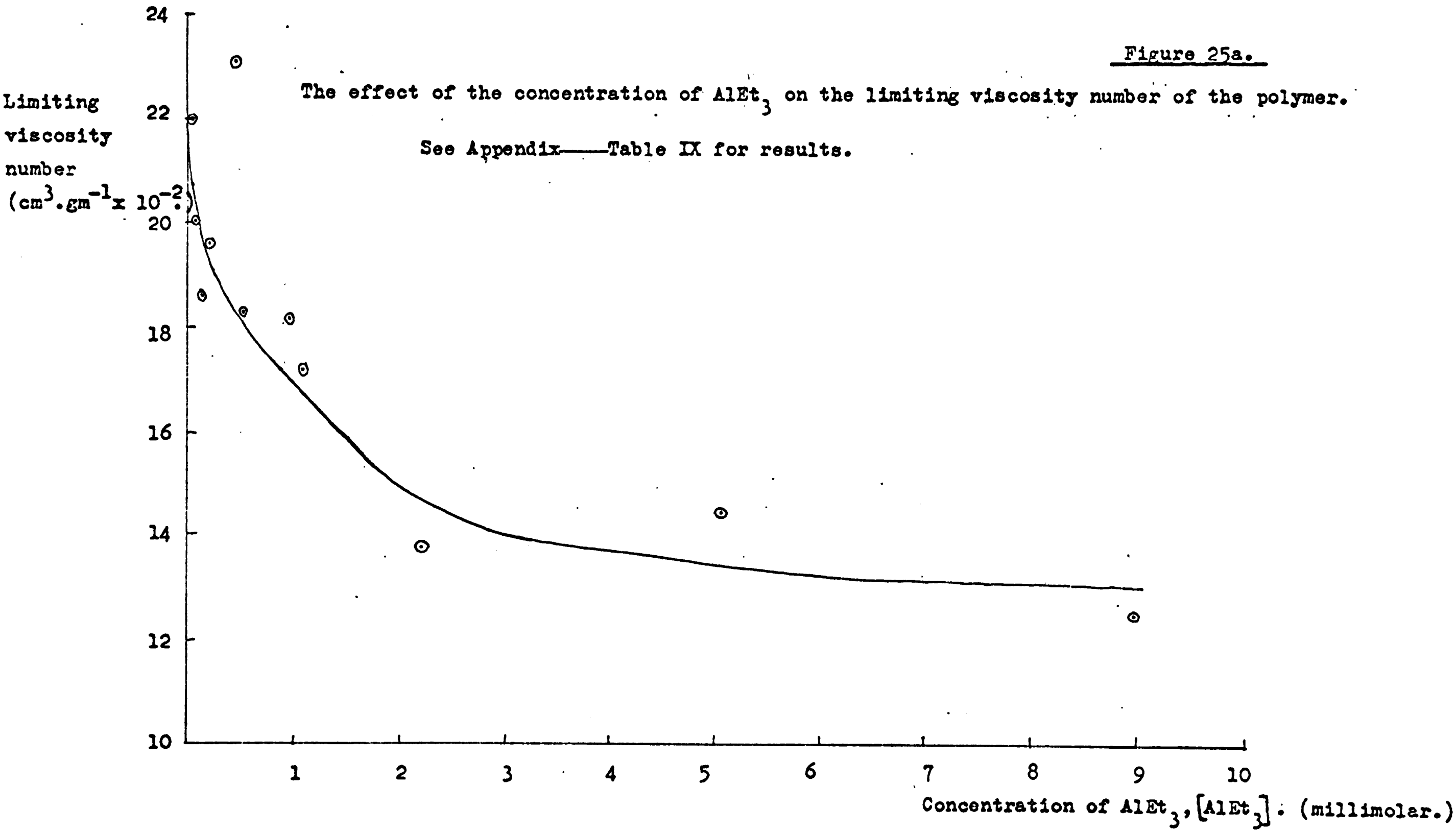
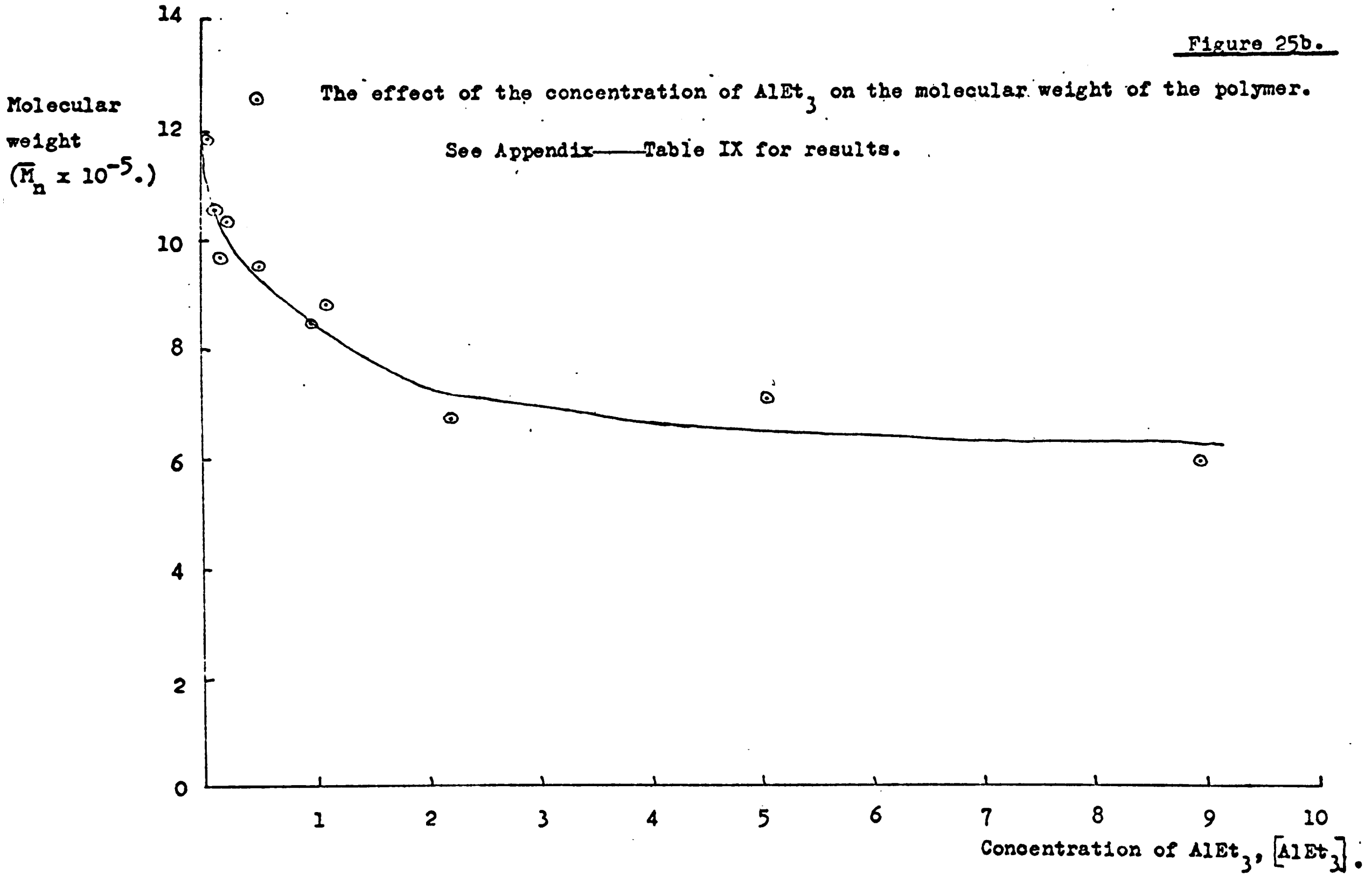


Figure 25b.

The effect of the concentration of $AlEt_3$ on the molecular weight of the polymer.

See Appendix——Table IX for results.



(iii) <u>The effect of titanium (III) chloride</u>

Table 9 shows the effect of various titanium (III) chloride catalyst concentrations upon the molecular weight of the polymer. It can be seen that there was no marked effect upon the molecular weight by the catalyst concentration. The results did not show any significant trend but were randomly distributed around a limiting viscosity number value of about 20.3 $cm^3 gm^{-1} \times 10^{-2}$ and $\bar{M}_n$ of about 10.7×10^5 with a scatter of $\sim \pm 20\%$.

Similar results were found by Grieveson[58] for ethylene polymerization by the γ-$TiCl_3/AlEt_2Cl$ system for variation in the $TiCl_3$ concentration from 1 - 8 millimolar. The result is also in agreement with the findings of McKenzie et al[60] who showed that the concentration of VCl_3 has no effect on the $\bar{M}_n$ of polymer formed from 4-methyl pentene-1 in the $VCl_3/Al(isobutyl)_3$ system. Natta et al[42] however have found conflicting results in the case of the polymerization of propylene with an α-$TiCl_3/AlEt_3$ catalyst system.

The decrease in $\bar{M}_n$ with increasing $[TiCl_3]$ observed by Natta may be the result of chain transfer reactions probably involving aluminium triethyl. At high $TiCl_3$ concentrations if the catalyst is starved of monomer this will reduce the propagation rate but not affect the chain transfer rate and the combination of the effects on these rates will result in a reduction of $\bar{M}_n$.

Table 9

Effect of titanium (III) chloride concentration on the number average molecular weight

Run No.	$[TiCl_3]$ millimolar	$[\eta]$ $cm^3 gm^{-1} \times 10^{-2}$	$\bar{M}_n \times 10^{-5}$
DK.14	.0500	19.61	10.31
DK.26	.0500	20.76	11.05
DK.15	.0200	17.56	9.01
DK.2	.0100	23.08	12.57
DK.7	.0100	18.29	9.47
DK.19	.0085	20.01	10.57
DK.16	.0050	18.26	9.45
DK.23	.0040	24.02	13.20
DK.20	.0030	19.44	10.20
DK.22	.0030	21.28	11.39
DK.21	.0020	22.57	12.24
DK.17	.0020	22.35	12.09
DK.24	.0015	19.38	10.16
DK.18	.0010	16.72	8.49
DK.29	.0010	20.96	11.18

(iv) Effect of temperature

The results for the effect of temperature upon molecular weight are shown in Figure 26. In the present system the assymptotic molecular weight was found to increase with temperature upto 30°C., then above this temperature fall steadily. Figure 27 shows a plot of $\log_{10}(\bar{M}_n)$ versus the reciprocal of the absolute temperature and also a comparative plot of $\log_{10}$(polymerization rate) versus 1/T.

Grieveson[58] found in the γ-$TiCl_3/AlEt_2Cl$ system which he studied that the molecular weight fell continuously between 0 and 70°C. and that the relationship between $\log \bar{M}_n$ and $10^3/T$ consisted of two linear regions changing in slope at about 50°C. Grieveson compared this change of slope in the $\bar{M}_n$ versus T relationship with the discontinuity in the relationship between polymerization rate and temperature which also occurred at a similar temperature, and concluded from this that the change in slope for $\log_{10} \bar{M}_n$ versus $10^3/T$ coincided with the onset of diffusion (mass transfer) control. As shown in Figure 27 the results in the present work do not show this correlation between the discontinuity in the molecular weight relationship and the reaction rate relationship. The factors influencing the reaction rate have been discussed earlier but the discontinuity in the molecular weight relation for this system is attributed to differences in activation energies for the chain transfer and chain propagation processes. It is considered that up to 30°C. little chain termination (i.e. either termination or transfer reactions) takes place

Figure 26a.

The effect of temperature on the limiting viscosity number of the polymer.

See Appendix——Table X for results.

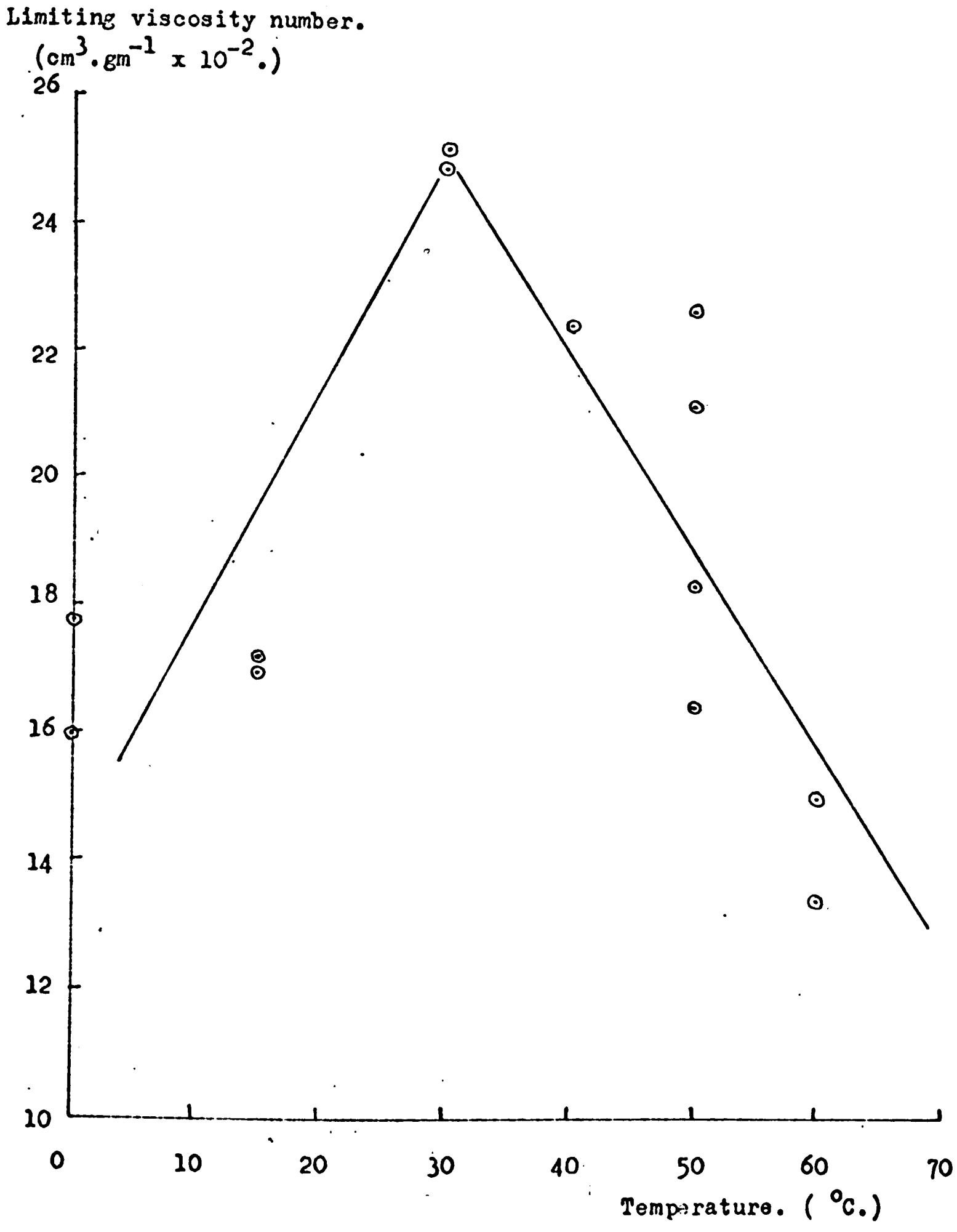
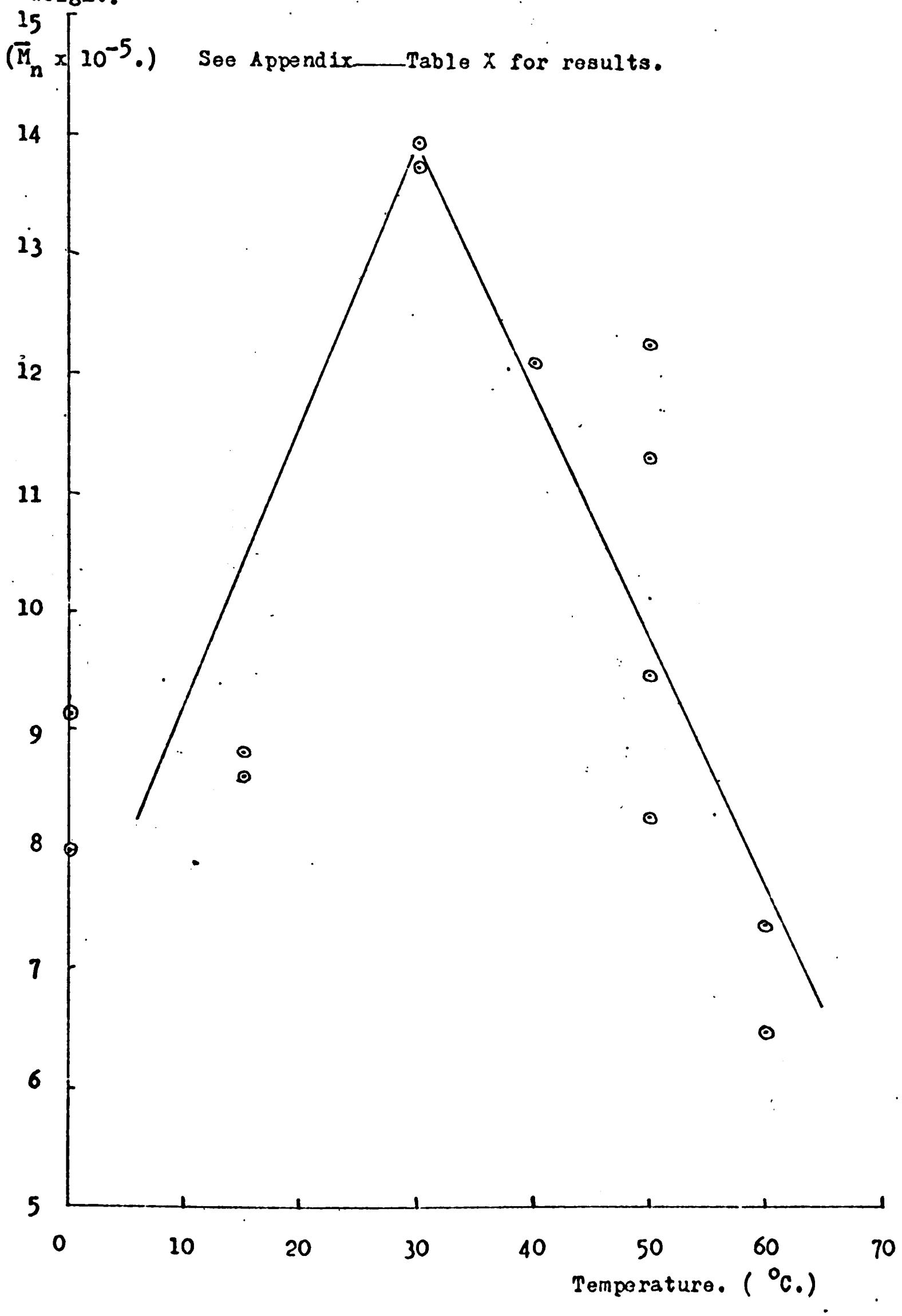


Figure 26b.

The effect of temperature upon the molecular weight of the polymer.



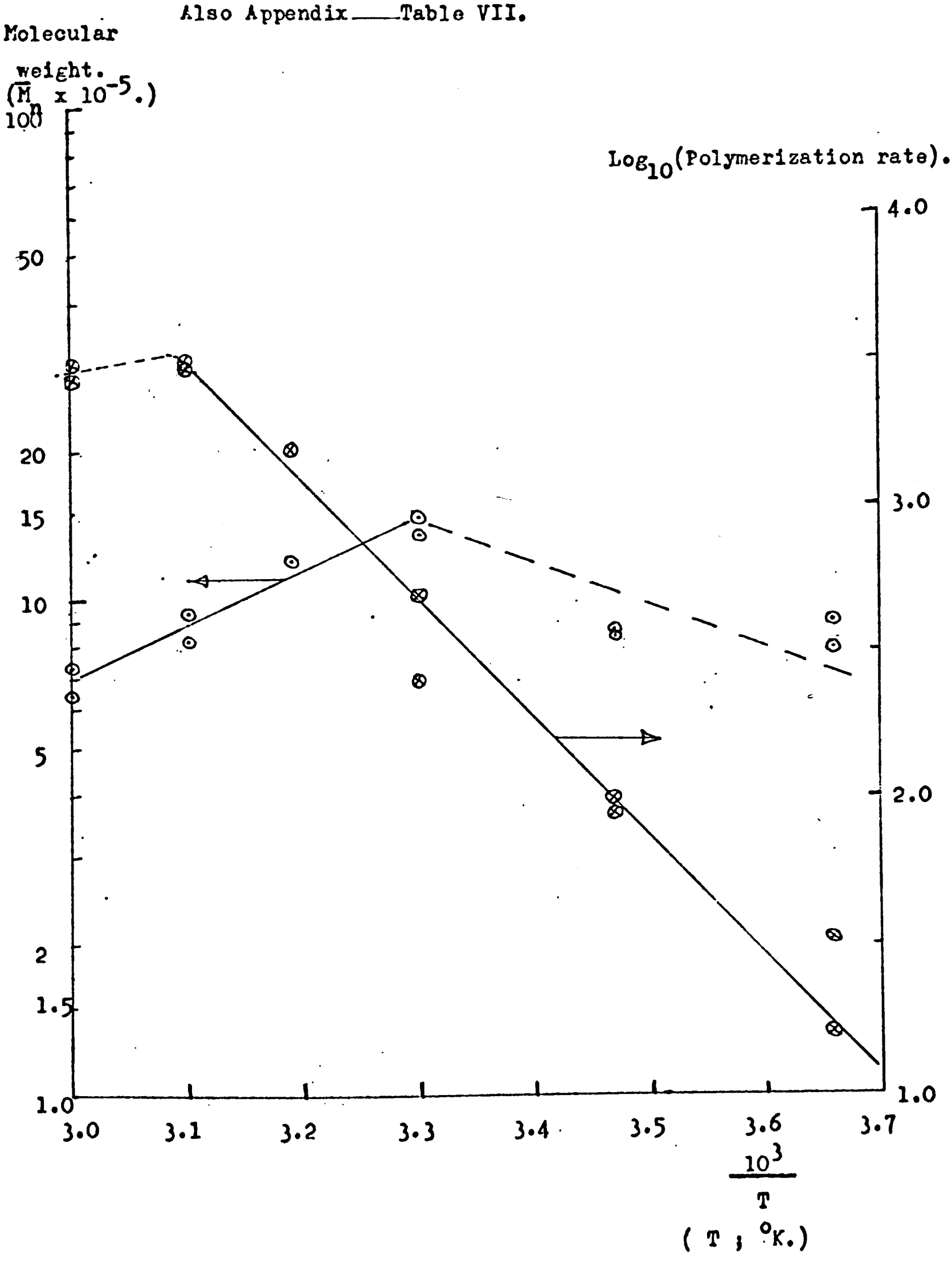
See Appendix——Table X for results.

Figure 27.

The effect of temperature on the molecular weight and on the polymerization rate.

See Appendix____Table X for results.

Also Appendix____Table VII.



as the energy of activation for chain termination is markedly higher than for propagation. However, for temperatures $>30^{o}C$. the effect of the termination reaction is believed to increase causing the fall in $\bar{M}_n$ values. McKenzie and Tait[60] found a similar effect at about $40^{o}C$., in the polymerization of 4-methyl pentene-1 with a VCl_3/Al(isobutyl)$_3$ system, which they attributed to this latter cause.

The results of Chirkov et al[65] support this proposal as they found activation energies of 70.3 kJ mole^{-1} (16.8 kcal mole^{-1}) and 111.7 kJ mole^{-1} (26.7 kcal mole^{-1}) for chain propagation and chain rupture reactions respectively.

Further support is given by the results quoted earlier where it was proposed that the more marked nature of the decay curve at higher alkyl concentrations might result from transfer reactions involving aluminium trialkyl. The present results suggest that similar transfer reactions might also occur involving the aluminium trialkyl at lower alkyl concentrations but higher temperatures. However, this does not take into account the part which chain termination reactions, such as transfer involving monomer, spontaneous termination and destructive termination (i.e. termination of active centres), might play.

(v) The effect of temperature upon the change in the number average molecular weight with time

The changes in the molecular weight versus time curves at various temperatures are shown in Figure 28. In these curves it will be seen that the limiting molecular weight attained rises from 0°C. to 30°C. but falls again from 30°C. to 50°C. The overall shape of the curve was similar for all temperatures investigated. However, it was found that the initial build up to the limiting condition appeared to be more gradual at the increased temperatures.

A comparative curve is shown in Figure 29 for an experiment using the γ-$TiCl_3/AlEt_2Cl$ catalyst system (similar to current commercial systems). This system was found to attain a higher limiting value of $\bar{M}_n$ than the organo-magnesium reduced $TiCl_3/Al(Et)_3$ system under equivalent conditions.

This result is in agreement with the findings of McKenzie and Tait[60] who found higher values of $\bar{M}_n$ were produced in the polymerization of 4-methyl pentene-1 by VCl_3 using aluminium diethyl chloride as co-catalyst than when using aluminium triethyl as co-catalyst.

(vi) The determination of active site concentration

The number of active sites actively participating in polymerization was determined using the following procedure. In order to measure the concentration of active sites the following assumptions were made concerning the kinetics of the polymerization.

It was assumed that:

(i) There is a steady state concentration $[C^*]$

Figure 28.

The variation of the molecular weight with time for the magnesium reduced catalyst system.

See Appendix——Table XI for results.

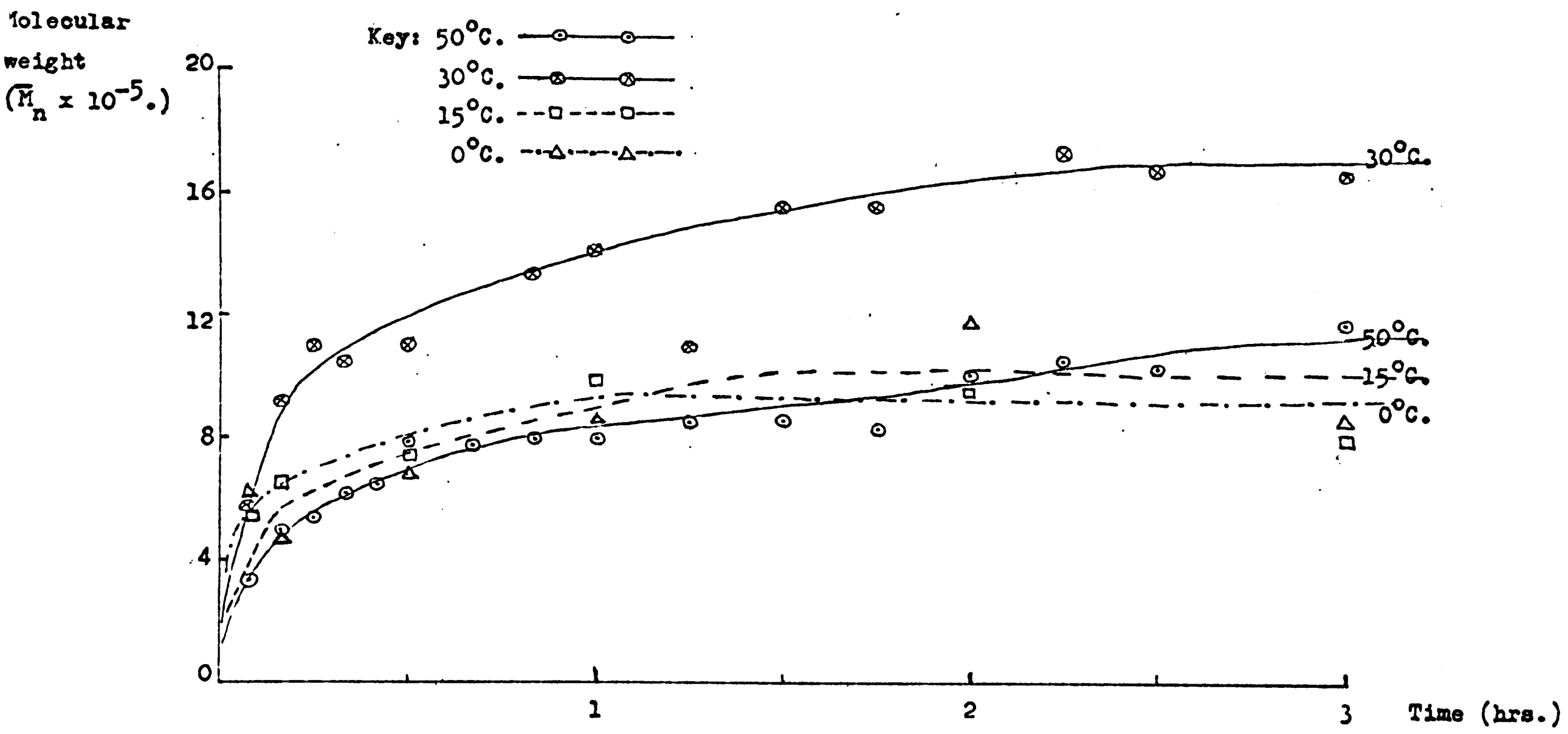
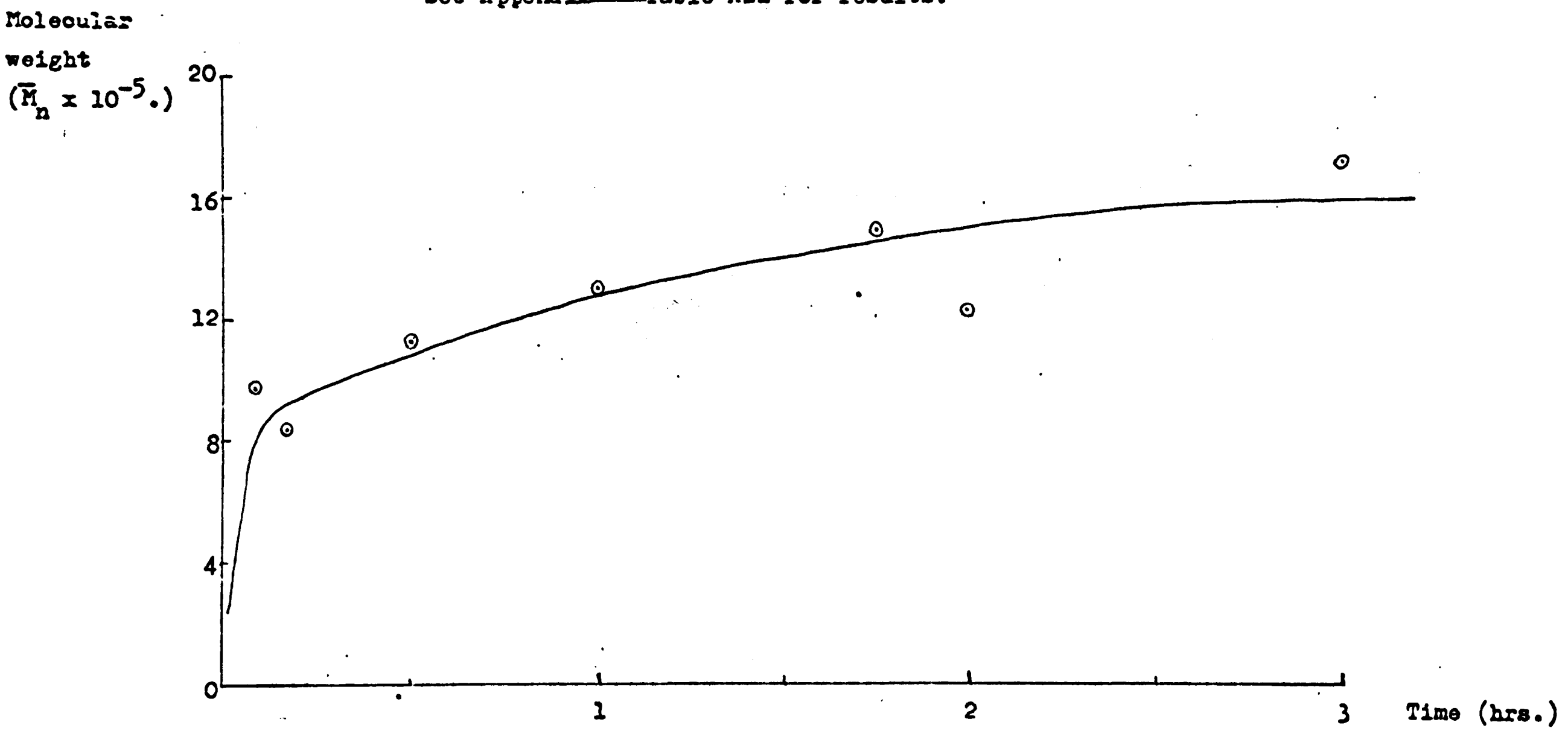


Figure 29.

The variation of the molecular weight with time for the conventional catalyst system at 50°C.

See Appendix——Table XII for results.



of active sites set up before the first sample is removed from the system, i.e. active sites are created rapidly at the start of the reaction and a steady state concentration is thereafter maintained.

$\frac{d[C^*]}{dt} = 0$ for all measured reaction times $t \geqslant 5$ mins.

(ii) Chain transfer and chain termination reactions occur without the destruction of activity, i.e. there is no catalyst deactivation during the reaction period under the conditions employed in the experiment.

As the mechanism of transfer is uncertain a first order constant is estimated for this Reaction Scheme:

(a) $C^*—P_{n-1} + M \xrightarrow{R_p} C^*—P_n$

where C^* is an active site

P_n is a growing polymer chain of n monomer units

M is a monomer molecule

R_p = Rate of chain propagation

Therefore, $R_p = k_p [C^*] [M]$

k_p = rate constant of propagation

$$k_p = \frac{R_p}{[C^*][M]} \quad ;.....(1)$$

(b) $C^* - P_n \xrightarrow{R_t} C^* + P_n$

where the activity of the site C* is retained.

R_t = rate of chain transfer.

Therefore, $R_t = k_t [C^*]$

$$k_t = \frac{R_t}{[C^*]} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Now if Y_t = yield of polymer (g) at time t.

$(\bar{M}_n)_t$ = number average molecular weight of polymer at time t.

N_t = Total number of polymer molecules plus total number of growing chains at time t (in moles)

then clearly,

$$N_t = \frac{Y_t}{(\bar{M}_n)_t}$$

Therefore in a plot of Y_t versus N_t, Y_t versus $Y_t/(\bar{M}_n)_t$

when $Y_t \longrightarrow 0$

as $t \longrightarrow 0$, $N_t \longrightarrow [C^*]$

(see assumption (i))

therefore the intercept of this plot $\doteqdot [C^*]$

Also:

At any time, since $R_{tot} = \frac{dY}{dt}$ where R_{tot} = measured rate of ethylene consumption.

$$\frac{dN}{dY} \cdot R_{tot} = \frac{dN}{dY} \cdot \frac{dY}{dt}$$

$$= \frac{dN}{dt}$$

$$= R_t$$

Using (2) $k_t = \frac{R_t}{[C^*]}$

$$\text{therefore, } k_t = \frac{\frac{dN}{dY} \cdot R_p}{[C^*]}$$

$$\text{also from (1) } k_p = \frac{R_p}{[C^*][M]}$$

Thus, from results of Yield, $\bar{M}_n$, and R_p the values of $[C^*]$, k_p, and k_t may be calculated.

Figures 30 to 34 show Y_t versus $Y_t/(\bar{M}_n)_t$ plots for the present system at 50°C., 30°C., 15°C. and 0°C. and also a comparative experiment using γ-$TiCl_3$-$AlEt_2Cl$ at 50°C.

The results at 50°C. and 30°C. show a linear relationship within the limits of experimental error, throughout the initial part of the reaction. The linear nature of the relationship enables k_t to be found by determination of the gradient dN_t/dY_t and also supports the assumption that $[C^*]$ is constant ($d[C^*]/d_t = 0$). At 15°C. and 0°C. the results are less conclusive, particularly as relatively few points were determined, and these show an appreciable amount of scatter between them. The results at 0°C. show better correlation than those at 15°C. but in both cases it is possible that the assumptions made concerning the reaction at 50°C. may be breaking down at these temperatures, e.g. an explanation of the results at 15°C. might be that the curvature of the plot is due to the generation of active sites. At 50°C. this is assumed to be rapid but at 15°C. this assumption may not be true. For completeness the results at 15°C. and 0°C. have been used in the determination of other reaction parameters but the above reservations must be borne in mind.

The concentrations of active sites as determined from

Figure 30.

Plot of $Y_t/(\overline{M}_n)_t$ versus Y_t for the magnesium reduced catalyst system at 50°C, (0.01 mM $TiCl_3$).

See Appendix——Table XIIIfor results.

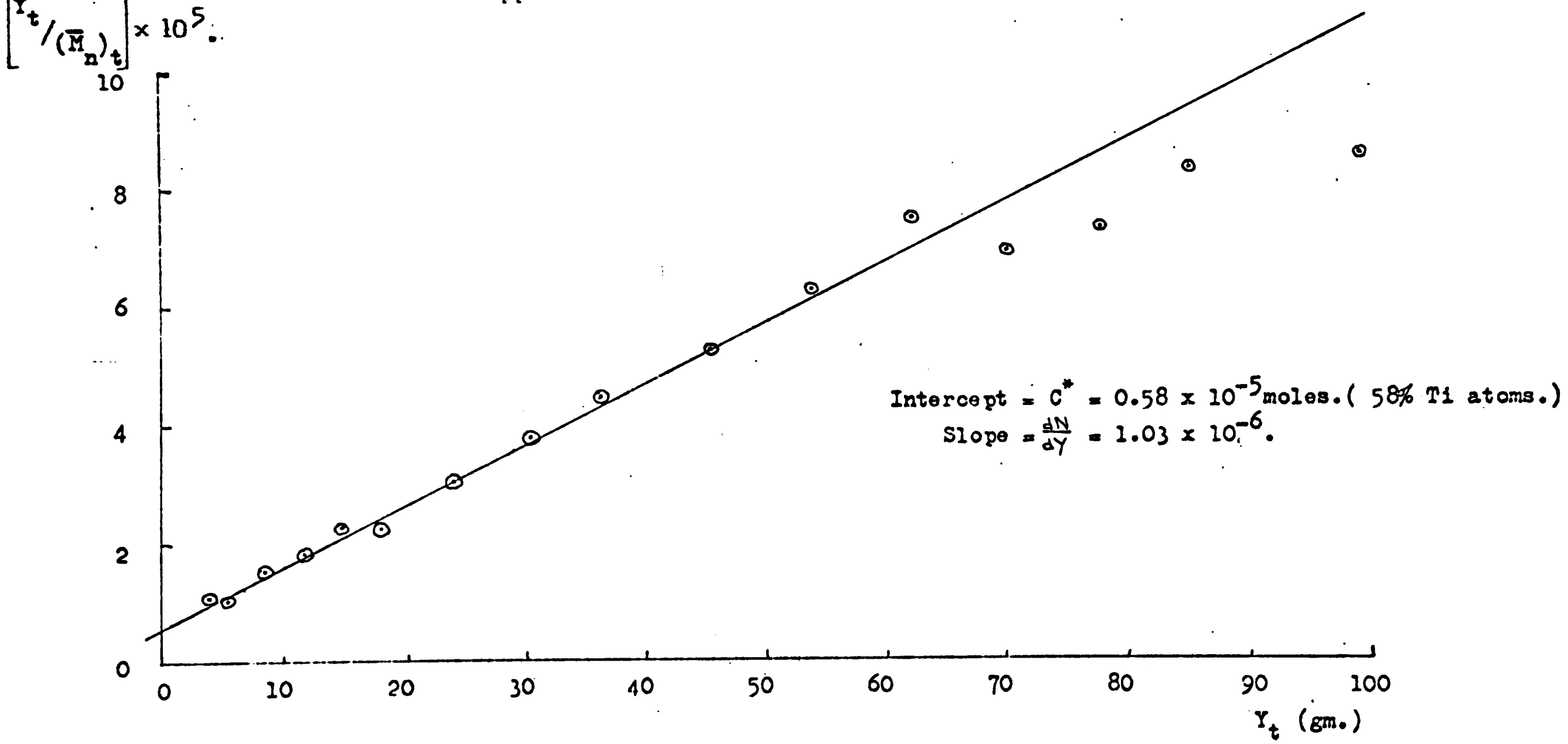


Figure 31.

Plot of $Y_t/(\overline{M}_n)_t$ versus Y_t for the magnesium reduced catalyst system at 30°C, (0.02 mM $TiCl_3$).

See Appendix——Table XIII for results.

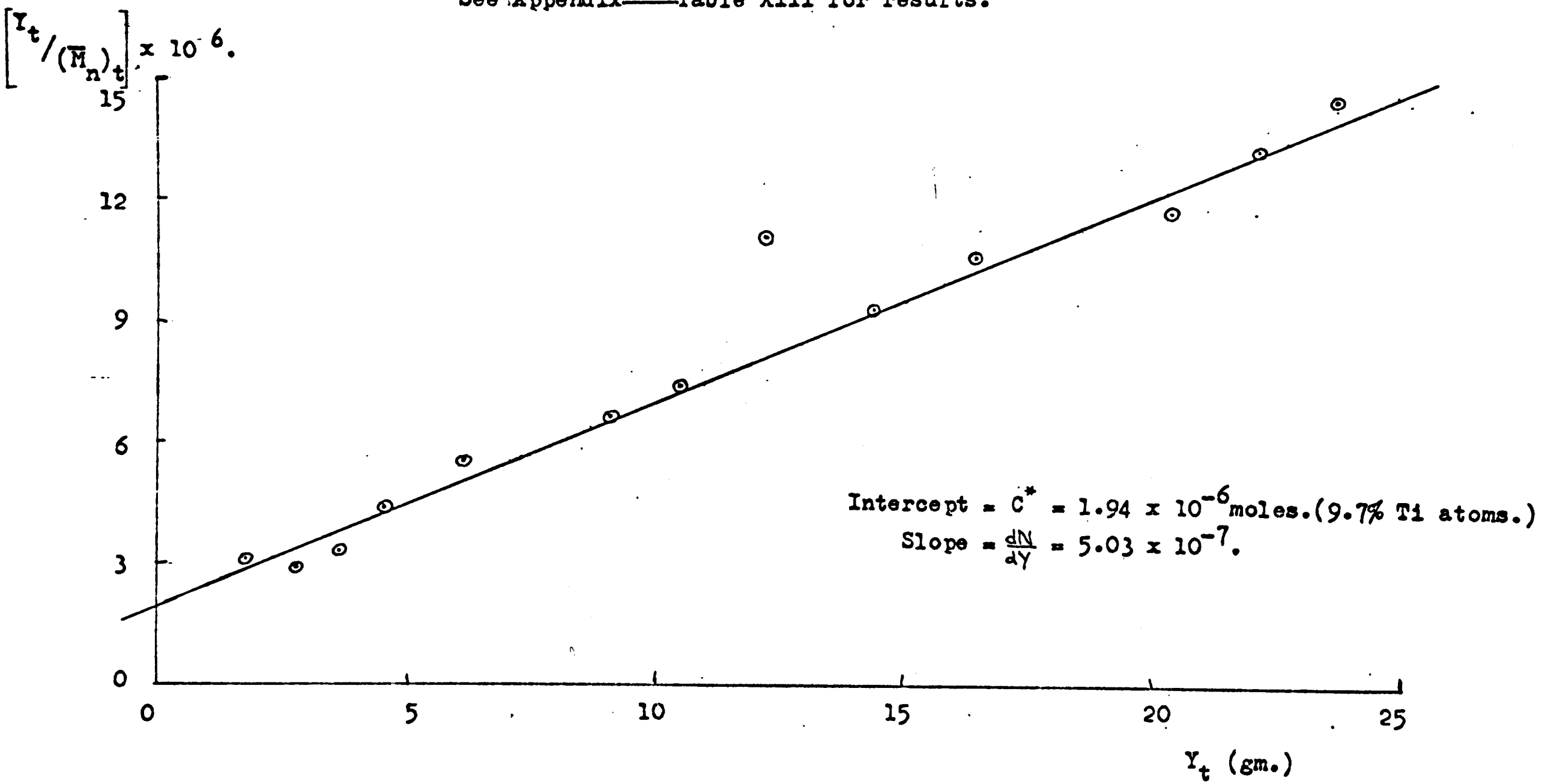
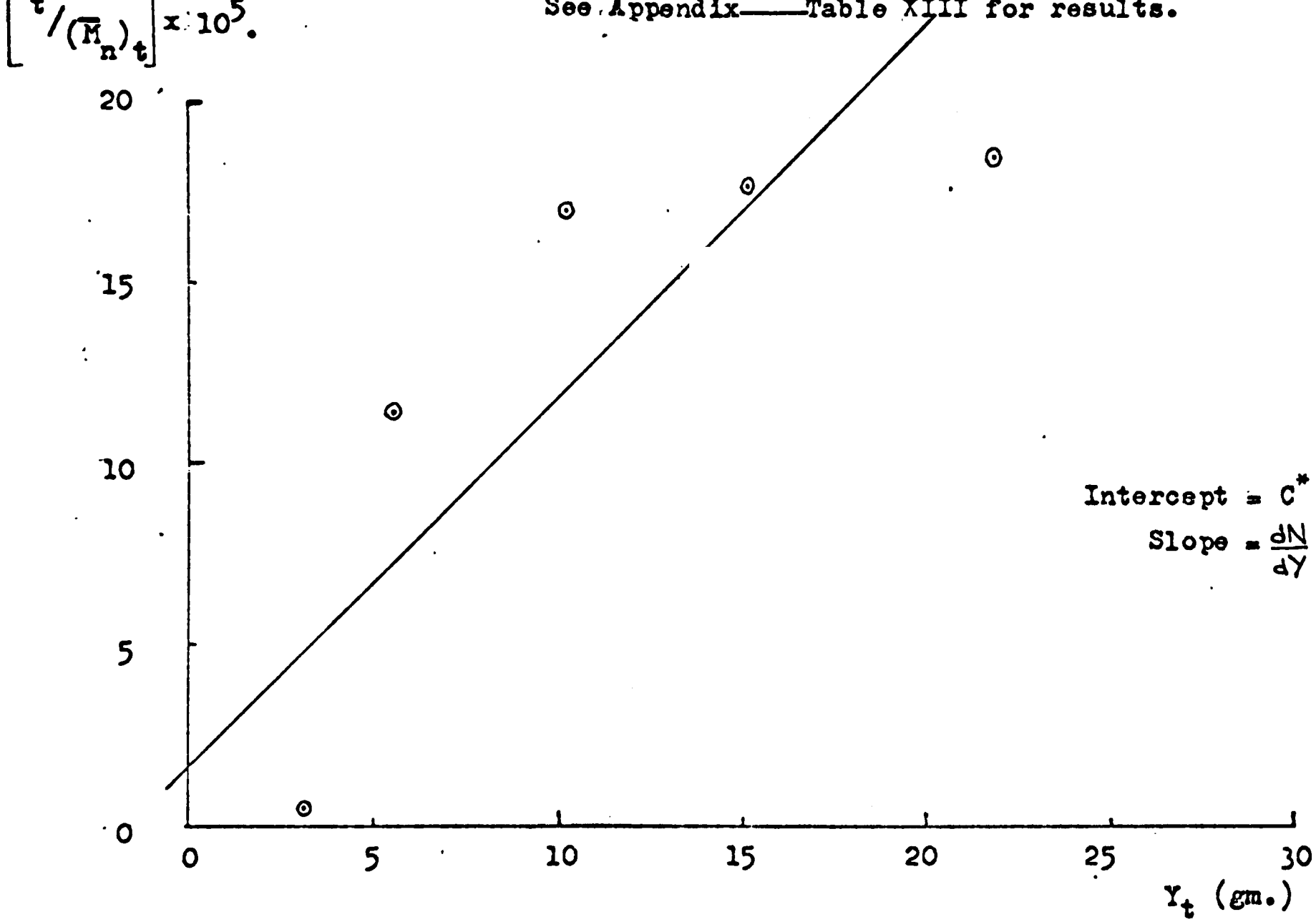


Figure 32.

Plot of $Y_t/(\overline{M}_n)_t$ versus Y_t for the magnesium reduced catalyst system at 15°C,(0.1 mM $TiCl_3$).

See Appendix——Table XIII for results.



Intercept = C^* = 1.7×10^{-6} moles.(1.7% Ti atoms.)

Slope = $\frac{dN}{dY}$ = 1.03×10^{-6}.

Figure 33.

Plot of $Y_t/(\overline{M}_n)_t$ versus Y_t for the magnesium reduced catalyst system at 0°C,(0.29 mM $TiCl_3$).

See Appendix——Table XIII for results.

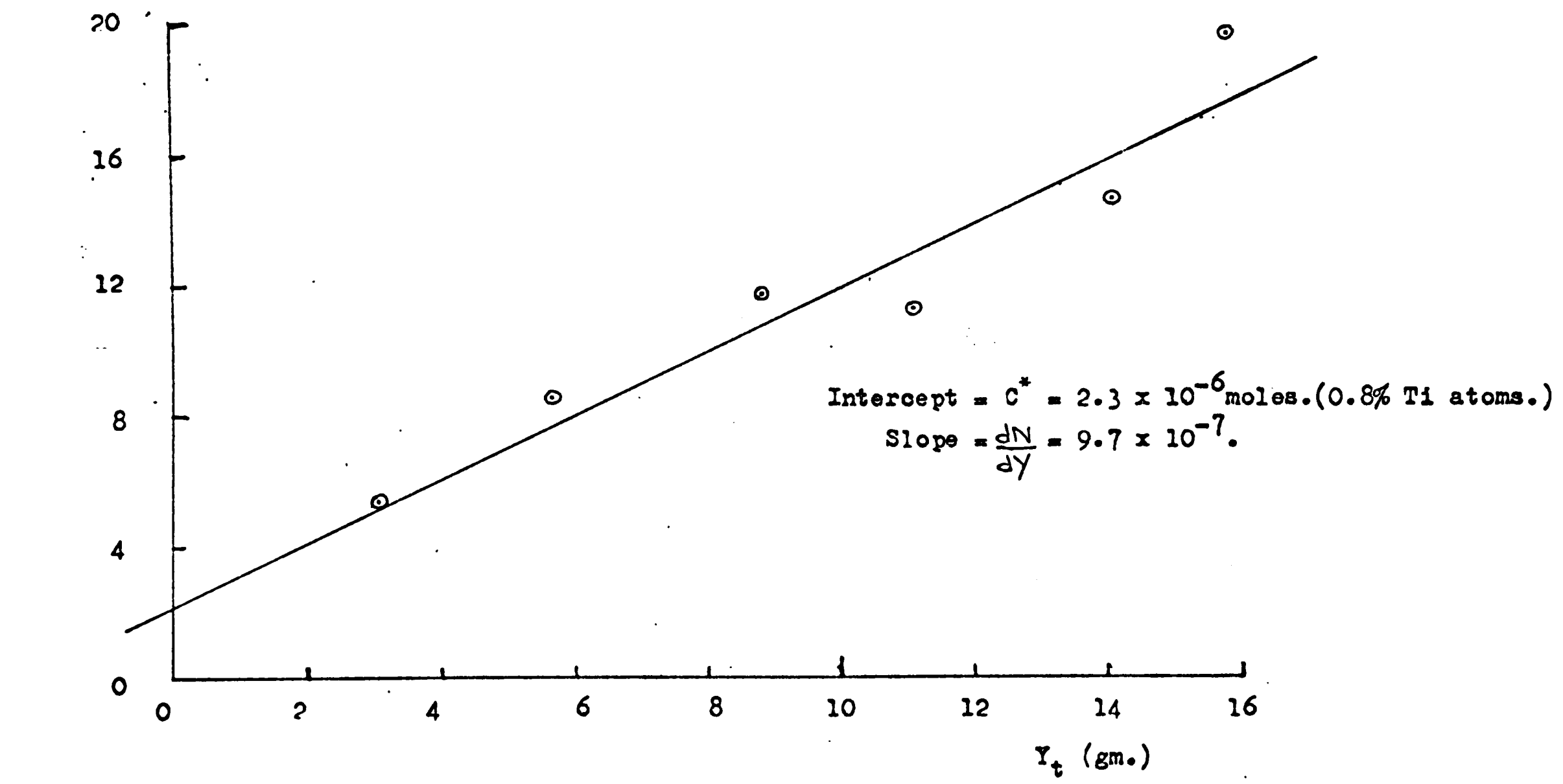
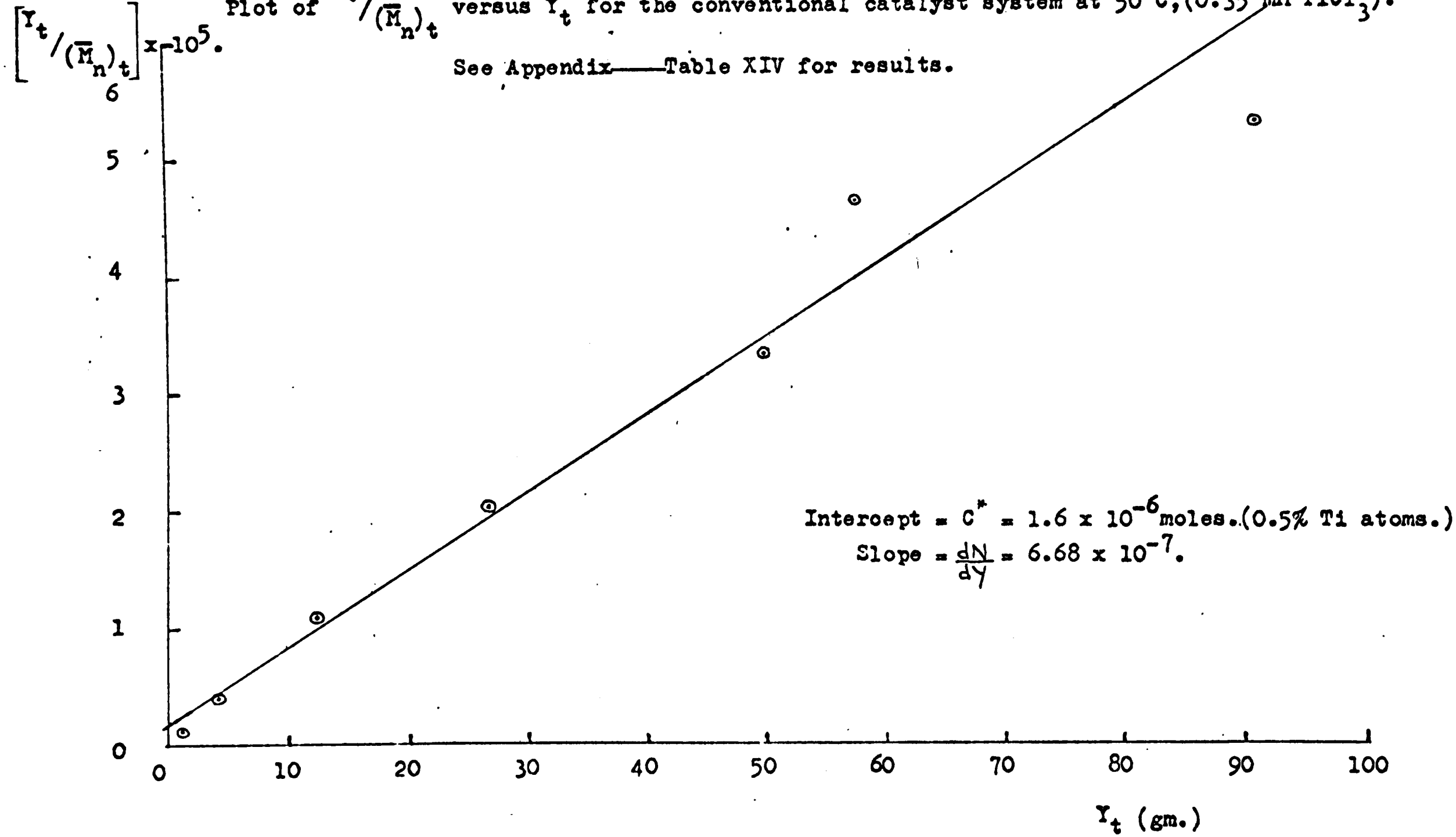


Figure 34.

Plot of $Y_t/(\overline{M}_n)_t$ versus Y_t for the conventional catalyst system at 50°C, (0.35 mM $TiCl_3$).

See Appendix——Table XIV for results.



Intercept = C^* = 1.6×10^{-6} moles. (0.5% Ti atoms.)

Slope = $\frac{dN}{dY} = 6.68 \times 10^{-7}$.

the intercepts of the $Y_t/(\bar{P}_n)_t$ vs. Y_t plots were as follows:

Dodecyl magnesium bromide prepared $TiCl_3/AlEt_3$

0.01 mM $TiCl_3$ at 50°C.

0.58 moles active sites per mole $TiCl_3$

(≈ 60% Ti atoms active)

0.02 mM $TiCl_3$ at 30°C.

0.097 moles active sites per mole $TiCl_3$

(≈ 10% Ti atoms active)

0.10 mM $TiCl_3$ at 15°C.

0.017 moles active sites per mole $TiCl_3$

(≈ 2% Ti atoms active)

0.286 mM $TiCl_3$ at 0°C.

0.0080 moles active sites per mole $TiCl_3$

(≈ 0.8% Ti atoms active)

Aluminium diethyl chloride prepared γ-$TiCl_3/AlEt_2Cl$

0.35 mM $TiCl_3$ at 50°C.

0.0046 moles active sites per mole $TiCl_3$

(≈ 0.5% Ti atoms are active)

These results are comparable to those reported by other authors for Ziegler systems. Grieveson[58] reported a value of ≈1.5% of the titanium atoms as active sites for ethylene polymerization at 40°C. using an aluminium triethyl prepared γ-$TiCl_3/AlEt_2Cl$ system. However, in the presence of 50% hydrogen in the ethylene feed Grieveson found only 0.5% of the titanium atoms were active. Schnecko et al[67] have shown that number of active sites in an γ-$TiCl_3$ system for propylene was dependent upon the technique of catalyst preparation.

Thus at least part of the differences found in a comparison of the results obtained with the γ-$TiCl_3/AlEt_2Cl$ used in these experiments with the results obtained by Grieveson is probably due to this cause. Feldman and Perry[68] polymerized ethylene with a $TiCl_4/AlR_3$ system in which they estimated the active centre concentration was between 0.003 mole/mole and 0.015 mole/mole, e.g. 0.011 at 55°C. and 0.05 at 40°C., which is also in fairly close agreement with our results for the γ-$TiCl_3/AlEt_2Cl$ system.

Comparison of the results obtained from the experiment using the aluminium diethyl chloride reduced γ-$TiCl_3/AlEt_2Cl$ system with those obtained using the dodecyl magnesium bromide reduced system shows that at 50°C. there are about 130 times more active sites present in the latter system. The active site concentration of the former system is comparable to that of the dodecyl magnesium bromide prepared system at 0°C. The results also confirm the findings of Chien[69] who gave evidence that the concentration of active centres in the propylene/$TiCl_3/AlEt_2Cl$ system increased with increasing temperature. The values of $1 \times 10^{-2} - 6 \times 10^{-1}$ mole(mole $TiCl_3)^{-1}$ found with this present system are substantially greater than those found with conventional $TiCl_3$ catalyst systems for ethylene polymerization $4 \times 10^{3} - 1.5 \times 10^{2}$ mole(mole $TiCl_3)^{-1}$. They are also substantially larger than values reported for $TiCl_3$ systems used for propylene polymerization where results of the order of $3 \times 10^{-3} - 1.0 \times 10^{-2}$ mole(mole $TiCl_3)^{-1}$ are found[44, 70, 71]. From the estimated values of the

active site concentration the rate constant k_p and k_t for chain propagation and chain termination were calculated as outlined previously.

$$k_p = \frac{R_{tot}}{[C^*][M]}$$

The following values* were found for k_p in the present work.

Dodecyl magnesium bromide prepared $TiCl_3/AlEt_3$

50°C.

1.70×10^6 dm^3 mole^{-1}hr.$^{-1}$

= 472 dm^3 mole^{-1}sec.$^{-1}$

30°C.

9.73×10^5 dm^3 mole^{-1}hr.$^{-1}$

= 270 dm^3 mole^{-1}sec.$^{-1}$

15°C.

1.11×10^6 dm^3 mole^{-1}hr.$^{-1}$

= 308 dm^3 mole-1sec.$^{-1}$

0°C.

4.1×10^5 dm^3 mole^{-1}hr.$^{-1}$

= 115 dm^3 mole^{-1}sec.$^{-1}$

Aluminium diethyl chloride prepared γ-$TiCl_3/AlEt_2Cl$

50°C.

5.73×10^6 dm^3 mole^{-1}hr.$^{-1}$

= 1592 dm^3 mole^{-1}sec.$^{-1}$

These results indicate that the catalytic activity of each of the sites found in the dodecyl magnesium bromide prepared $TiCl_3$ catalyst is only one-third of that found in

* See Appendix - note 3 for values of M and R_{tot} for these calculations.

the aluminium diethyl chloride prepared γ-$TiCl_3$ when the catalysts are used at 50°C. The increased rate, almost 40 times that of the conventional catalyst, with the dodecyl magnesium bromide prepared $TiCl_3$ is due to the concentration of active centres in the latter being almost 130 times greater than for the aluminium diethyl chloride reduced case.

However, the value found for k_p as estimated above is substantially larger than that found by other authors. Grieveson[58] found a value of k_p 80 $dm^3 mole^{-1} sec.^{-1}$ for the polymerization of ethylene using the aluminium triethyl reduced γ-$TiCl_3/AlEt_2Cl$ system in a cyclohexane diluent at 40°C. This estimate is about twenty times smaller than that found in the present work for aluminium diethyl chloride prepared γ-$TiCl_3/AlEt_2Cl$ at 50°C.

$$k_t = \frac{dN}{dY} \frac{R_{tot}}{[C^*]}$$

The following values* were found for k_t in the present work.

Dodecyl magnesium bromide prepared $TiCl_3/AlEt_3$

50°C.

$$0.21 \text{ hr.}^{-1}$$

$$= 5.8 \times 10^{-5} \text{ sec.}^{-1}$$

30°C.

$$0.073 \text{ hr.}^{-1}$$

$$= 2.0 \times 10^{-5} \text{ sec.}^{-1}$$

15°C.

$$0.19 \text{ hr.}^{-1}$$

$$= 5.3 \times 10^{-5} \text{ sec.}^{-1}$$

*See Appendix - Note 3 for values of R_{tot} and note 4 for values of $\frac{dN}{dY}$.

$0^{o}C.$

$$0.079 \text{ hr.}^{-1}$$

$$= 2.2 \times 10^{-5} \text{ hr.}^{-1} \text{ sec.}^{-1}$$

Aluminium diethyl chloride prepared γ-$TiCl_3/AlEt_2Cl$

$50^{o}C.$

$$0.45 \text{ hr.}^{-1}$$

$$= 1.3 \times 10^{-4} \text{ sec.}^{-1}$$

The k_t value determined for the aluminium diethyl chloride prepared γ-$TiCl_3/AlEt_2Cl$ system has been compared to k_m, the rate constant for chain transfer with monomer evaluated by Grieveson for the $TiCl_3/AlEt_2Cl$/Ethylene system[58].

Assuming that the major contribution to the chain transfer rate constant in the comparative systems is made by chain transfer to monomer and contributions from all other chain transfer and termination processes are small in comparison then

$$k_m = \frac{k_t}{[M]}$$

Thus k_m in the present case for the γ-$TiCl_3/AlEt_2Cl$ system at $50^{o}C.$ is 1.1×10^{-3} dm^3 $mole^{-1}sec.^{-1}$ compared with $k_m = 1 \times 10^{-2}$ dm^3 $mole^{-1}sec.^{-1}$ at $40^{o}C.$ for the similar γ-$TiCl_3/AlEt_2Cl$ system found by Grieveson. The value we find for the γ-$TiCl_3/AlEt_2Cl$ system is ~10 times smaller than in the results found by Grieveson and 20 times smaller for the magnesium alkyl reduced $TiCl_3/AlEt_3$ system.

The value found in the present case for the $TiCl_3/AlEt_3$ system at $50^{o}C.$ is about half that found for the γ-$TiCl_3/AlEt_2Cl$ system.

(vii) The lifetime of growing polymer chains

The average value for the lifetime of the growing polymer chains was calculated using the expression:

$$L = \frac{\bar{P}_n \, C^*}{R_p}$$

where L = average lifetime of growing polymer chain.

P_n = number average degree of polymerization.

R_p = Rate of polymerization.

As $\bar{P}_n = \frac{\bar{M}_n}{28}$ for any time t, $\bar{M}_n$ was taken to be the number average molecular weight at the end of the polymerization experiment (i.e. when t = 3 hours).

The following values* were found for L in the present work.

Dodecyl magnesium bromide prepared $TiCl_3/AlEt_3$

50°C.

9.7 mins.

30°C.

25 mins.

15°C.

13 mins.

0°C.

24 mins.

Aluminium diethyl chloride prepared γ-$TiCl_3/AlEt_2Cl$

50°C.

4.5 mins.

*See Appendix – Note 5 for $\bar{M}_{nt}$ = 3 hours and $\bar{P}_n$ values, also Note 3 for R_p values.

These results show that the lifetime of the growing polymer chain is shorter for the aluminium diethyl chloride prepared γ-$TiCl_3/AlEt_2Cl$ system than for the present system at 50°C. by a factor of 2. The results also show that the lifetime of the growing polymer increases as the temperature of the reaction decreases.

Comparison of the results for the γ-$TiCl_3/AlEt_2Cl$ system with those of Grieveson for a similar system[58] show the estimate of the lifetime is markedly shorter in the present work, 4.5 mins. compared with 30 mins. in the Grieveson case. However, in the case of polymerization using a 50-50 ethylene-hydrogen feed, which Grieveson also investigated, a comparable figure of 7 mins. is found. This system has a similar concentration of active sites 0.5% Ti atoms to the $TiCl_3/AlEt_2Cl$ system used in the present work. The result for the conventional catalyst in the present work is also comparable to the results of Feldman and Perry[68] who polymerized ethylene using a $TiCl_4/AlR_3$ system. They observed chain lifetimes of 2 - 30 minutes typically 4 min. but increasing with reaction time, and Chien[72] found lifetimes of 24 mins. for ethylene polymerization by titanium dicyclopentadienyl dichloride/$AlMe_2Cl$ at temperatures between 0°C. - 30°C. Natta[44] found similar lifetimes (5 - 15 mins.) for growing chains in the α-$TiCl_3/Al(Et)_3$/propylene system. Various other authors have found considerably longer lifetimes of the order of several hours for both the polymerization of ethylene and of propylene by Ziegler systems[49, 69, 73].

CHAPTER IV

Summary

The results obtained in this work indicate that the original objective of preparing an ultra-high molecular weight polyethylene material for use in artificial hip-joints has been reached. It has been shown possible to polymerize ethylene to a material having $[\eta] \geqslant 25$ $cm^3 gm^{-1} \times 10^{-2}$ at exceptionally high yields. For example, polymer yields of 50 kg/g $TiCl_3$ can be typically obtained with ethylene at atmospheric pressure and 500 kg/g $TiCl_3$ with ethylene at 10 atmospheres total pressure. In order to obtain such results reagents of exceptionally high purity were required and procedures were developed to ensure low impurity levels <2 ppm. Under optimum polymerization conditions a yield of $>14{,}000$ kg/g $TiCl_3$ has been obtained. These high catalytic activities and low reagent impurity levels have produced polyethylene with a very low heavy metal content; typically polymers with titanium analysis $\leqslant 1$ ppm Ti.being realized. This means that the present material shows a reduction of titanium content compared with the commercial products Hifax and Hostalen of 150 times and and 10 times respectively. Investigations into the wear rate of the present material are still being carried out and the results of these tests will confirm whether this material has the anticipated improvement in this characteristic.

The polymerization reaction was characterised by the following sequence of events. Initially before polymerization

occurred the catalyst material was present as very fine brown particles which were so finely dispersed as to impart only faint colouration to the diluent at the catalyst concentrations normally employed. As polymerization occurred the diluent became turbid by the formation of a colloidal suspension of polymer particles which precipitated when the particle size increased forming discrete visible particles. These tended to aggregate on further growth but finally the aggregates broke down to give a slurry which consisted of a uniform dispersion of fine white particles.

It was observed that the limiting viscosity number of the polymer increased as the pressure of the ethylene employed during the reaction increased.

Investigation of the effect of aluminium triethyl concentration, [Al], at constant $TiCl_3$ concentration showed that low rates of polymerization were produced at low aluminium triethyl concentrations. At high aluminium triethyl concentrations the maximum rate appeared to be relatively independent of the concentration of aluminium triethyl up to the limit investigated. However, the decay period was found to be more marked at higher alkyl concentrations. It was considered that a minimum aluminium triethyl concentration was required to activate polymerization, probably by alkylation, and that high aluminium triethyl concentrations probably gave rise to chain termination processes involving transfer or termination reactions with aluminium triethyl.

For variation in the concentration of the $TiCl_3$ catalyst component at constant aluminium triethyl

concentration, a linear proportionality was observed between the $TiCl_3$ concentration and the polymerization rate for $[TiCl_3] < 0.02$ millimolar. A first order reaction with respect to the $TiCl_3$ concentration was indicated and the results were in accordance with the proposal generally employed in Ziegler systems that

$$C^* \propto [TiCl_3]$$

Mass transport was considered to become the rate limiting process for $[TiCl_3] > 0.02$ millimolar and a method has been employed whereby this effect has been eliminated in the evaluation of a maximum rate and maximum rate constant. The values for these parameters in the present system operating at atmospheric pressure and 50°C. are:

Maximum rate:

971.7 mole ethylene $(g\ TiCl_3)^{-1} hr.^{-1}$ $atmosphere^{-1}$

27,200 g ethylene $(g\ TiCl_3)^{-1} hr.^{-1}$ $atmosphere^{-1}$

Maximum rate constant:

8057 moles ethylene (mole ethylene in satd. soln.)

8057 gms. ethylene (gm ethylene in satd. soln.)$(g\ TiCl_3)^{-1} hr.^{-1}$ $atmosphere^{-1}$

The relationship between reaction temperature and polymerization rate was investigated and the rate was observed to rise sharply to an apparent maximum at 50°C. and then flatten off for a further increase in temperature. This

discontinuity could possibly be attributed to mass transport rate limitations or the alternative explanation that at higher temperatures catalyst deactivation occurs causing a fall in the number of active sites. The overall apparent activation energy obtained from the Arrhenius plot was found to be 75.7 $kJ.mole^{-1}$ (18.1 $Kcal.mole^{-1}$) which is higher than has been reported by other authors for ethylene polymerization using similar Ziegler systems.

A relationship providing an approximate estimation of the number average molecular weight has been applied to calculate values of $\bar{M}_n$ from $[\eta]$ in the investigation of the molecular weight behaviour of the polymerization reaction. Comparative results are given for the estimation of the molecular weight by the above technique using viscometry measurements and for estimations from the results of gel permeation chromatography.

Investigation of the molecular weight behaviour during polymerization showed that $\bar{M}_n$ built up to a limiting value of $\sim 1 \times 10^6$ over a period of 2 - 3 hours for polymerizations at 50°C. and atmospheric pressure with $TiCl_3$ concentration 0.01 millimolar and $AlEt_3$ concentration 0.5 millimolar.

It was found that the molecular weight was dependent upon the aluminium triethyl concentration, $\bar{M}_n$ decreasing as $[AlEt_3]$ increased. This effect was interpreted as probably arising from chain transfer involving the aluminium triethyl.

The concentration of $TiCl_3$ catalyst component was found to have no significant effect upon the molecular weight. The results showed a random scatter, attributed to

experimental variations, of $\sim\pm 20\%$ about a mean value of 1.1×10^6.

The molecular weight was found to initially increase with temperature up to 30°C. then to decrease for temperatures >30°C. This effect was attributed to the greater importance of chain termination reactions at temperatures >30°C.

The molecular weight versus reaction time curves were found to show relatively little variation with temperature. The limiting value of $\bar{M}_n$ reached was found to increase between 0°C. and 30°C. but to decrease from 30°C. to 50°C. The build up region of the curve was found to be more gradual at higher temperatures.

A method has been proposed and used for the determination of the concentration of active sites, C*, from the kinetic rate and molecular weight data. These data were also used to estimate values of k_p, k_t and L, the chain propagation rate constant, the chain termination rate constant and the average lifetime of growing polymer chains respectively. The results obtained for these parameters are shown in Table 10.

The values found for C* indicate that there are about 130 times the number of active sites involved in polymerization in the magnesium reduced system compared to those in a conventional γ-$TiCl_3/AlEt_2Cl$ catalyst. However, values of k_p indicate that each active site in the magnesium reduced system apparently has a lower intrinsic catalytic activity as the chain propagation rate constant for this

system is only approximately one-third of that found for the conventional γ-$TiCl_3/AlEt_2Cl$ catalyst.

The average lifetime of the growing polymer chain was estimated at between 10 minutes and 25 minutes for the magnesium reduced system increasing in length as the temperature decreased from 50°C. to 0°C. In the case of the γ-$TiCl_3/AlEt_2Cl$ system a shorter lifetime of the order of 5 mins. at 50°C. was estimated about half the value found for the magnesium reduced system at the same temperature. The results indicate that the enhanced activity found in the magnesium reduced system can be attributed to a larger proportion of active sites than is found with conventional catalysts. The overall improvement in the catalytic activity arises from this difference, although it is not as large as might be expected, considering the activity of sites in a conventional catalyst.

Schnecko et al[67] have previously reported that the active site concentration can be dependent upon the method of catalyst preparation. As in the case of alkyl aluminium prepared catalysts, where the aluminium compounds produced in the reduction can be incorporated into the catalyst particles[74], it has been suggested that magnesium residues from the preparation are incorporated into catalyst particles. The ionic radius of magnesium (0.065 nm.) is closer in size to that of titanium (0.068 nm.) than that of aluminium (0.05 nm.) from which it can be predicted that the substitution of magnesium for titanium in any lattice formation should occur more readily than aluminium.

Roper[50] proposed that catalyst preparations involving

Table 10

Values obtained for the kinetic parameters investigated in this work

System.	Concentration of active sites C* mole active (mole $TiCl_3$)$^{-1}$	Propagation rate constant k_p dm^3 mole^{-1} sec.$^{-1}$	Termination rate constant k_t sec.$^{-1}$	Ave. chain lifetime L mins.
Magnesium reduced catalyst with $AlEt_3$				
at 50°C.	0.580	472	5.8×10^{-5}	9.7
at 30°C.	0.097	270	2.0×10^{-5}	25
at 15°C.	0.017	308	5.3×10^{-5}	12
Aluminium reduced catalyst with $AlEt_2Cl$				
at 50°C.	0.005	1592	1.3×10^{-4}	4.5

Grignard reagents as used in the present work involved a "co-crystallisation" of magnesium halide and titanium (III) chloride which can be expected to produce a material of very disordered structure like that of a glass. X-ray diffraction observations cited by Roper confirm that disorder was present in $TiCl_3$ prepared using the alkyl magnesium halide method.

This information can be considered in the light of the findings of Rodriguez and van Looy[75] and other authors who report that the active polymerization sites in conventional catalysts occurred at the edges of crystals and at crystal defects in the crystalline particles.

If the observations of Schnecko et al[67] that as the size of $TiCl_3$ crystals decrease the number of active sites

increases and correspondingly the activity increases are also noted, it may be concluded that a high concentration of active sites and therefore high activity should be expected from a catalyst with a very disordered structure.

An alternative proposal made by Roper[50] is that magnesium atoms incorporated into catalyst particles might act as promoters through the chlorine atoms. Roper based his proposal for this mechanism upon the findings of Cossee concerning the action of aluminium in aluminium chloride as a catalyst promoter. As the propagation rate found in the present work for the magnesium reduced system is lower than that found with the conventional catalyst, it is considered unlikely that a mechanism of this nature is operative.

The comparison of results found in the present work for the values of $[C^*]$, k_p, k_t, and L found in the γ-TiCl/$AlEt_2Cl$/ethylene system with those found in a similar system investigated by Grieveson shows marked discrepancies. As the concentration of active sites, $[C^*]$, has been used in the present work in the evaluation of all the remaining parameters cited above, it is of paramount importance that the determination of $[C^*]$ is accurate. The discrepancies found between the present work and that of other authors may arise from limitations in the accuracy of the method used to determine $[C^*]$ in the present work, e.g. the assumed applicability of the relationship between $[\eta]$ and M_n for all polymer samples and the assumptions made concerning the reaction kinetics. It is suggested that

further investigations should be carried out in order to estimate the active site concentration by a more direct method such as a radio-chemical one.

If a suitable method for the direct determination of the active site concentration can be found, the variation in this parameter can be observed for variations in the concentrations of the monomer, the aluminium alkyl andthe titanium (III) chloride. Observations confirming the results found for variation in $[C^*]$ with temperature could also be confirmed.

The present work has not established the relationship between $\overline{M}_n$ and the monomer concentration and also R_{tot} and the monomer concentration which should be determined for a complete kinetic investigation of the system. Limited experiments were conducted in the early work into the effect of different aluminium alkyls on the rate of polymerization and the number average molecular weight of the polymer. The results of these experiments appear to indicate that the order of greatest polymerization rate is $AlEt_3 > Al(iB)_3 > Al(n\text{-}oct)_3$ and the order of highest limiting molecular weight is $Al(n\text{-}oct)_3 > AlEt_3 > Al(iB)_3$.

Further investigations can be carried out to confirm these observations and to extend them to other aluminium alkyls.

The further investigations outlined above would complete the data on the kinetic features of the reaction. At this stage it could be seen whether the results found for the magnesium reduced catalyst system conformed to the general kinetic schemes currently proposed for Ziegler

catalyst systems, and also the mechanisms proposed for the reactions involved.

A field of investigation as yet virtually unexplored for the magnesium reduced catalyst is its catalytic activity in the polymerization of other monomers particularly propylene and buta-1,3-diene. Investigations in this area can not only realise more information concerning those properties of the catalyst already investigated for the ethylene case but will also discover any capability the system has for the preparation of stereoregular polymers. This latter information would be of academic interest and if this catalyst can be successfully used for the preparation of isotactic polypropylene at increased yields or rates, it could also have important commercial implications. Another obvious extension of research into the magnesium reduced system would be the preparation of copolymers by this method.

REFERENCES

1. H. von Pechmann, Chem. Ber., 31, 2643 (1898).

2. G. D. Buckley, C. H. Cross and N. H. Ray, J. Chem. Soc., 2714 (1950).

3. W. H. Carothers, J. W. Hill, J. E. Kirby and R. A. Jacobson, J. Am. Chem. Soc., 52, 5279 (1930).
   H. R. Arnold and E. C. Herrick (to E. I. du Pont de Nemours & Co., Inc.), U.S. Patent 2,726, 218 (1955).

4. E. W. Fawcett and R. O. Gibson, J. Chem. Soc., 386,(1934).
   H. Staudinger, Trans. Faraday Soc., 32, 97 (1936).
   (p.119 - Remarks of E. W. Fawcett in general discussion following the above paper).

5. E. W. Fawcett, R. O. Gibson, M. W. Perrin, J. G. Paton and E. G. Williams (to Imperial Chemical Industries Ltd.), Brit. Patent 471,590 (1936).
   E. W. Fawcett, R. O. Gibson and M. W. Perrin (to Imperial Chemical Industries, Ltd.), U.S. Patent 2,153,553 (1936) and U.S. Patent 2,188,465 (1936).

6. K. Ziegler, E. Holzkamp, H. Breil and H. Martin, Angew. Chemie, 67, 426 (1955) and Angew. Chemie, 67, 541 (1955).
   K. Ziegler and H. Martin, Makromol. Chemie, 19, 186 (1956).
   K. Ziegler, Belg. Patent 533,362 (1954).

7. A. Clark, J. P. Hogan, R. L. Banks and W. C. Lanning, Ind. Eng. Chem, 48, 1152 (1956).
   R. Hayes and W. Webster, Plastics Institute, Transations, 32, 219 (1964).
   J. P. Hogan and R. L. Banks (to Phillips Petroleum Co.), U.S. Patent 2,825,721 (1958).

8. H. L. Hooe, Modern Plastics International Encyclopaedia, 78 (1972-73).

9. E. F. Peters, A. Zletz and B. L. Evering, Ind. Eng. Chem., 49, 1879 (1957).

E. F. Peters and B. L. Evering (to Standard Oil Co. of Indiana), U.S. Patent 2,658,059 (1953).

U.S. Patent 2,692,261 (1954).

A. Zletz (to Standard Oil Co. of Indiana),

U.S. Patent 2,692,257 (1954).

A. K. Roebuck and A. Zletz (to Standard Oil Co. of Indiana),

U.S. Patent 2,696,258 (1954).

U.S. Patent 2,780,617 (1957).

10. E. Field and M. Feller, Ind. Eng. Chem., 49, 1883 (1957).

E. Field and M. Feller (to Standard Oil Co. of Indiana),

U.S. Patent 2,691,647 (1954).

U.S. Patent 2,726,234 (1955).

U.S. Patent 2,726,231 (1955).

U.S. Patent 2,731,452 (1956).

U.S. Patent 2,731,453 (1956).

U.S. Patent 2,791,576 (1957).

U.S. Patent 2,834,769 (1958).

E. Field and W. E. Kuentzel (to Standard Oil Co. of Indiana), U.S. Patent 2,631,091 (1953).

11. M. Fischer (to Badische Anilin & Soda Fabrik A.G.),

German Patent 874,215 (1953).

12. M. J. Roedel (to E. I. du Pont de Nemours & Co., Inc.),

U.S. Patent 2,462,678 (1949).

U.S. Patent 2,475,520 (1949).

12. continued..

U.S. Patent 2,497,323 (1950).

U.S. Patent 2,511,480 (1950).

U.S. Patent 2,762,791 (1956).

U.S. Patent 2,983,704 (1961).

13. G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti and G. Moraglio, J. Am. Chem. Soc., 77, 1708,(1955).

14. G. Natta, J. Polymer Sci., 16, 143 (1955).

G. Natta and P. Corradini, Makromol. Chemie, 16, 77 (1955).

G. Natta, Angew. Chemie, 68, 393 (1956).

15. G. Natta and P. Corradini, Rend. Accad. Naz. Lincei., (8), 19, 229 (1955).

16. G. Mazzanti, A. Valvassori andG. Pajaro, Chimica e Industria, 39, 733 (1957). Chimica e Industria, 39, 743 (1957).

17. W. R. Sorenson and T. W. Campbell, Preparative Methods of Polymer Chemistry, Interscience, New York, Second Ed., 1968, Chapter 4, Section VIII, p.287.

18. P. A. Gautier, S. Mostert and H. Verbrugge (to Shell Internationale Research Maatschappij N.V.), Brit. Patent 1,139,450 (1969).

19. D. C. Smith, Ind. Eng. Chem., 48, 1161 (1956).

20. J. Charnley, Lancet, 1129 (1961).

21. J. Charnley, J. Bone and Joint Surgery, 54B, 61 (1972).

22. J. T. Scales and S. A. Lowe, Engng. Medicine, 1, 52 (1972).

23. P. S. Walker, Engng. Medicine, 1, 91 (1972).

24. G. C. Pratt, Plastics Institute, Transactions, 32, 255 (1964).

25. G. Natta and G. Mazzanti, Tetrahedron, 8, 86 (1960).

26. J. Boor, Macromolecular Reviews, 2, 115 (1967).

27. C. D. Nenitzescu, C. Huch and A. Huch, Angew. Chemie, 68, 438 (1956).

28. F. J. Carol and W. L. Carrick, J. Am. Chem. Soc., 83, 2654 (1961).

29. P. Cossee, Trans. Faraday Soc., 58, 1226 (1962).

30. P. Cossee, J. Catalysis, 3, 80 (1964).

31. J. Boor and E. A. Youngman, J. Polymer Sci., B, 2, 265 (1964), J. Polymer Sci., B, 4, 913 (1965).

32. J. Boor, Ind. Eng. Chem. Prod. Res. and Dev., 9, 437 (1970).

33. R. N. Haward and A. N. Roper (to Shell Research Limited), German Patent 2,003,075 (1969) (Brit. Patent Appln. 3956/69). German Patent 2,061,487 (1971) (Brit. Patent Appln. 15945/70).

34. A. I. Vogel, A Textbook of Practical Organic Chemistry, Longmans, London, Third Ed., 1956, Chapter 3, Preparation 36, p. 280.

35. A. I. Vogel, A Textbook of Practical Organic Chemistry, Longmans, London, Third Ed., 1956, Chapter 3, Preparation 8, p. 237.

36. L. I. Zakharkin, O. Yu. Okhlobystin and B. N. Strunin, Tetrahedron Letters, 14, 631 (1962).

37. D. Bryce Smith and B. T. Blues, Chem. and Ind., 50, 1533 (1960).

38. I.U.P.A.C., J. Polymer Science, 8, 257 (1952).

39. P. F. Onyon, Techniques of Polymer Characterization, Ed. P. W. Allen, Butterworths, London,1959, Chapter 6, p.171.
Ch'ien Jên-Yüan, Determination of Molecular Weights of High Polymers, Israel Program for Scientific Translations, Jerusalem,1963, Chapter 2, p.29.

40. G. Boocock and R. N. Haward, Soc. Chem. Ind. (London), Monograph 20, 3 (1966).

41. M. N. Berger and B. M. Grieveson, Makromol. Chemie, 83, 80 (1965).

42. G. Natta, J. Polymer Sci., 34, 21 (1959).
G. Natta, I. Pasquon, A. Zambelli and G. Gatti, J. Polymer Sci., 51, 387 (1961).

43. T. Keii, Kinetics of Ziegler-Natta polymerization, Chapman and Hall, London,1972, Chapter 2, p.15 and Chapter 5, p.129.

44. G. Natta and I. Pasquon, Advances in Catalysis, 11, 1 (1959).

45. J. Boor and E. A. Youngman, J. Polymer Sci., B, 2, 265 (1964).

46. J. Boor and E. A. Youngman, J. Polymer Sci., B, 4, 913 (1966).

47. A. K. Ingberman, I. J. Levine and R. J. Turbett, J. Polymer Sci., A1, 4, 2781 (1966).

48. J. Ambroz, P. Osecky, P. Mejzlik and O. Hamrick, J. Polymer Sci., C. 16, 423 (1967).

49. M. N. Berger, G. Boocock and R. N. Haward, Advances in Catalysis, 19, 211 (1968).

50. R. N. Haward, A. N. Roper and K. L. Fletcher, Polymer, 14, 365 (1973).

51. I. D. McKenzie, P. J. T. Tait and D. R. Burfield, Polymer, 13, 307 (1972).

52. C. F. Feldman and E. Perry, J. Polymer Sci., 46, 217 (1960).

K. Fukui, T. Kagiya, S. Machi, T. Schimidzu and S. Yuasa, Bull. Chem. Soc. Japan, 35, 303 (1962).

J. C. W. Chien, J. Am. Chem. Soc., 81, 86 (1959).

C. E. H. Bawn and R. Symcox, J. Polymer Sci., 34, 138 (1959).

53. K. Fukui, T. Kagiya, S. Machi, T. Schimidzu and S. Yuasa, Bull Chem. Soc. Japan, 35, 306 (1962).

54. J. H. Elliott, K. H. Horowitz and T. Hoodock, J. Appl. Polymer Sci., 14, 2947 (1970).

55. H. Staudinger and W. Meuex, Ber. Deutsch. Chem. Ges., 63, 222 and 721 (1930).

56. H. Mark, Der Fest Korper, Leipzig (1938).

R. Houwink, J. Prakt. Chem., 157, 15 (1940).

57. M. O. De la Cuesta and F. W. Billmeyer, J. Polymer Sci., A, 1, 1721 (1963).

58. B. H. Grieveson, Makromol. Chemie, 84, 93 (1965).

59. A. D. Caunt, J. Polymer Sci., C, 4, 49 (1964).

60. I. D. McKenzie and P. J. T. Tait, Polymer, 13, 510 (1972).

61. H. Schnecko, K. Weirauch, N. Reinmoller, V. Bednjagin and W. Kern, Makromol. Chemie, 82, 156,(1965).

62. J. Boor, J. Polymer Sci., C, 1, 237,(1963).

63. D. R. Burfield and P. J. T. Tait, Polymer, 13, 215 (1972).

64. D. R. Burfield, P. J. T. Tait and I. D. McKenzie, Polymer, 13, 321 (1972).

65. L. A. Novokshonova, V. I. Tsvetkova and N. M. Chirkov, Izvestia Akad. Nauk SSSR Ser. Khim., 7, 1176 (1963).

66. E. Duch and L. Küchler, Z. Elektrochem., Ber. Bunsenges. Physik. Chem., 60, 218 (1956).

67. H. Schnecko, W. Dost and W. Kern, Makromol Chemie, 121, 159 (1969).

68. C. F. Feldman and E. Perry, J. Polymer Sci., 46, 217 (1960).

69. J. C. W. Chien, J. Polymer Sci., A, 1, 425 (1963).

70. V. Kissin, S. M. Mezhikovsky and N. M. Chirkov, European Polymer J., 6, 267, (1970).

71. R. W. Coover, J. E. Guillett, R. L. Combs and F. S. Joyner, J. Polymer Sci., A-1, 4, 2583 (1966).

72. J. C. W. Chien, J. Am. Chem. Soc., 81, 86 (1959).

73. G. Bier, W. Hoffman, G. Lehmann, and G. Seydel, Makromol. Chemie, 58, 1 (1962).

74. G. Natta, P. Corradini, G. Allegra, J. Polymer Sci., 51, 399 (1961).

75. L. A. M. Rodriguez and H. M. van Looy, J. Polymer Sci., A-1, 4, 1971 (1966).

APPENDIX

Notes

1. The concentration of ethylene in iso-octane was estimated by extrapolation of data for the solubility of ethylene in C_6 and C_7 hydrocarbons to a C_8 hydrocarbon. In this instance the value for the ethylene concentration was estimated at:

   0.12 moles ethylene-dm^3 iso-octane at 50°C.

2. Units of $1.0 \times 10^{-2} cm^3 gm^{-1}$ have been used throughout this text for the values of viscosity number and limiting viscosity number (L.V.N.) whilst units of $1.0 \times 10^{-2} gm.cm^3$ have been used for all the concentrations involved in the viscometry work. This means that all the numerical values of viscosity number and L.V.N. are equivalent to values expressed in the older Intrinsic Viscosity units ($dl.gm.^{-1}$). This allows direct comparison with the majority of reference material which is normally available in these units. All the following equations involving L.V.N. expressed as $[\eta]$ assume the use of these units.

3. Values estimated for the concentration of ethylene in iso-octane (see also Appendix - Note 1).

   0.12 moles ethylene-dm^{-3} iso-octane at 50°C.

   0.15 moles ethylene-dm^{-3} iso-octane at 30°C.

   0.17 moles ethylene-dm^{-3} iso-octane at 15°C.

   0.20 moles ethylene-dm^{-3} iso-octane at 0°C.

   Values of R_{tot} used to evaluate rate parameters:

Magnesium reduced catalyst.

at 50°C. R_{tot} = 1.183 mole ethylene $hr.^{-1}(0.01\ mM\ TiCl_3)^{-1}$

at 30°C. R_{tot} = 0.283 mole ethylene $hr.^{-1}(0.02\ mM\ TiCl_3)^{-1}$

at 15°C. R_{tot} = 0.320 mole ethylene $hr.^{-1}(0.10\ mM\ TiCl_3)^{-1}$

at 0°C. R_{tot} = 0.188 mole ethylene $hr.^{-1}(0.286\ mM\ TiCl_3)^{-1}$

Aluminium reduced catalyst.

at 50°C. R_{tot} = 1.101 mole ethylene $hr.^{-1}(0.35\ mM\ TiCl_3)^{-1}$

4. Values of $\frac{dN}{dY}$ obtained from figures 30 to 34.

Magnesium reduced catalyst.

at 50°C. $\frac{dN}{dY} = 1.03 \times 10^{-6}$

at 30°C. $\frac{dN}{dY} = 5.03 \times 10^{-7}$

at 15°C. $\frac{dN}{dY} = 1.03 \times 10^{-6}$

at 0°C. $\frac{dN}{dY} = 9.70 \times 10^{-7}$

Aluminium reduced catalyst.

at 50°C. $\frac{dN}{dY} = 6.60 \times 10^{-7}$

5. Limiting values for $\bar{M}_n$ were estimated from Figures 30 to 34. Using the plot of Nt/Yt where $Nt = Yt/\bar{M}_n$, the limiting value was taken to be $\bar{M}_n = Yt/Nt$ from the graphical plot where Yt had the value at which t = 3 hours.

Limiting values of $\bar{M}_n$.

Magnesium reduced catalyst.

at 50°C. $\bar{M}_n = 0.92 \times 10^6$

at 30°C. $\bar{M}_n = 1.71 \times 10^6$

at 15°C. $\bar{M}_n = 1.11 \times 10^6$

at 0°C. $\bar{M}_n = 0.90 \times 10^6$

Aluminium reduced catalyst.

at 50°C. $\bar{M}_n = 1.44 \times 10^6$

Values of Pn .

Magnesium reduced catalyst.

at 50°C. $\bar{P}n = 3.29 \times 10^4$

at 30°C. $\bar{P}n = 6.12 \times 10^4$

at 15°C. $\bar{P}n = 3.95 \times 10^4$

at 0°C. $\bar{P}n = 3.20 \times 10^4$

Aluminium reduced catalyst.

at 50°C. $\bar{P}n = 5.13 \times 10^4$

Table I

The effect of pressure upon viscosity number

Results shown in Figure 14.

Run No.	Slurry % weight	Pressure $Nm^{-2} \times 10^{-5}$		Viscosity Number $cm^3 gm^{-1} \times 10^{-2}$	Bulk Density $gmcm^{-3}$
		Total	Gauge		
OP39	20	1.0	Atmospheric	19	0.26
OP63	26	5.8	4.8	22	0.21
OP60	23	7.8	6.8	24	0.23
OP64	20	9.0	8.0	26	0.21
OP67	23	10.0	9.0	27	0.21

All the above experiments were carried out at 50°C. for 3 hours using a aluminium triethyl/titanium (III) chloride ratio of 1×10^2. The titanium (III) chloride was prepared using octyl magnesium bromide.

Table II

The absorption of ethylene versus time.

Results shown in Figure 15.

Time,	Total ethylene absorbed (dm^3 ethylene at S.T.P.)			
	Run No.: D.K.2	D.K.7	D.K.20	D.K.22
	$FiCl_3$ Concn: (0.01 mM)	(0.01 mM)	(0.003 mM)	(0.003 mM)
0	-	-	-	-
5	1.85	2.97	0.73	0.42
10	3.60	4.18	1.38	1.22
15	5.53	6.77	1.93	1.92
20	7.38	9.26	2.54	2.62
25	-	11.75	3.16	3.35
30	11.64	14.23	3.80	4.13
35	-	16.72	4.44	4.90
40	16.10	19.21	5.06	5.66
45	-	21.79	5.79	6.44
50	20.74	24.27	6.46	7.25
55	22.97	26.66	7.13	8.04
60	25.43	29.15	7.80	8.85
65	-	31.64	8.47	9.62
70	29.66	34.02	9.14	10.40
75	-	36.42	9.81	11.16
80	34.48	38.58	10.49	11.92
85	-	40.92	11.16	12.65
90	39.30	43.25	11.89	13.36
100	-	47.73	13.31	14.78
105	46.38	-	-	-
110	-	52.01	14.75	16.11

CONTD...

Table II (Contd.)

120	53.07	56.20	16.17	17.38
135	58.83	62.35	18.23	19.17
150	65.16	68.33	20.10	20.89
165	70.84	74.01	21.68	22.59
180	76.32	79.52	22.72	24.16

All the above polymerizations were carried out at 50°C. and atmospheric pressure using a 0.5 mMolar concentration of a aluminium triethyl and dodecyl magnesium bromide prepared $TiCl_3$.

Table III

Rate of absorption of ethylene versus time

Results shown in Figure 16.

Time min.	Rate of ethylene absorption (dm^3 ethylene at S.T.P. $hr.^{-1}$)		
	Run No.: / $TiCl_3$ concn.:	D.K.7 (0.01 mM)	D.K.22 (0.003 mM)
0		-	-
5		35.66	5.02
10		14.67	9.64
15		31.00	8.42
20		29.83	8.42
25		29.83	8.74
30		29.83	9.38
35		29.83	9.14
40		29.83	9.14
45		31.00	9.38
50		29.83	9.70
55		28.66	9.46
60		29.83	9.70
65		29.83	9.30
70		28.66	9.30
75		28.66	9.22
80		26.02	9.06
85		28.03	8.82
90		28.03	8.50
100		26.87	8.50
110		25.70	7.97

CONTD....

Table III (Contd.)

120		25.12	7.65
135		24.61	7.15
150		23.90	6.89
165		22.74	6.80
180		22.03	6.27

All the above polymerizations were carried out at 50°C. and atmospheric pressure using a 0.5 mMolar concentration of aluminium triethyl and dodecyl magnesium bromide prepared $TiCl_3$.

Table IV

Rate of absorption of ethylene versus time at different aluminium triethyl concentrations

Results shown in Figure 18

Time	Rate of ethylene absorption (dm^3 ethylene at S.T.P.-$hr.^{-1}$		
	Run No.	D.K.6	D.K.7	D.K.3
	$AlEt_3$ concn.	(0.06 mM)	(0.5 mM)	(5.05mM)
0		-	-	
5		12.20	35.66	32.14
10		-	14.67	36.78
15		18.65	31.00	35.23
20		17.70	29.83	33.69
25		18.81	29.83	32.14
30		22.13	29.83	33.69
35		21.02	29.83	24.41
40		21.02	29.83	27.08
45		22.13	31.00	-
50		21.02	29.83	25.43
55		21.02	28.66	-
60		19.91	29.83	20.77
65		21.02	29.83	16.23
70		21.02	28.66	-
75		19.92	28.66	16.56
80		18.81	26.02	14.94
85		17.70	28.03	-
90		17.70	28.03	12.77
100		14.94	26.37	10.31

CONTD...

Table IV (Contd.)

110	12.18	25.70	11.59
120	6.10	25.12	9.41
135	2.97	24.61	6.06
150	2.60	23.90	6.01
165	-	22.74	4.51
180	0	22.03	3.48
$R_{max.}$	21.6	30.3	36.8

All the above polymerisations were carried out at 50°C. and atmospheric pressure using aluminium triethyl and a 0.01 mMolar concentration of dodecyl magnesium bromide prepared $TiCl_3$.

Table V

Rate of absorption versus aluminium triethyl concentration

Results shown in Figure 19

Run No.	Aluminium triethyl concentration, (millimolar)	Max. ethylene absorption rate (dm^3 ethylene at S.T.P.-$hr.^{-1}$)
DK.6	0.06	21.6
DK.5	0.11	22.5
DK.12	0.15	21.3
DK.11	0.22	28.4
DK.2	0.48	29.3
DK.7	0.53	30.3
DK.8	1.10	33.2
DK.9	2.20	31.2
DK.3	5.05	36.8
DK.4	8.96	30.7

All the above polymerizations were carried out at 50°C. and atmospheric pressure for 3 hours using aluminium triethyl and a 0.01 mMolar concentration of dodecyl magnesium bromide prepared $TiCl_3$.

Table VI

Rate of absorption of ethylene versus titanium (III) chloride concentration

Results shown in Figures 20 and 21.

Run No.	$TiCl_3$ concn. (millimolar), Ti	Max. ethylene absorption rate, R, (dm^3 ethylene at S.T.P.-$hr.^{-1}$)	$1/_{Ti}$	1/R
DK.26	0.05	109	20	0.009
DK.15	0.02	66.9	50	0.015
DK.25	0.02	60.9	50	0.016
DK.2	0.01	29.3	100	0.034
DK.7	0.01	30.3	100	0.033
DK.19	0.0085	23.9	118	0.042
DK.16	0.0050	17.1	200	0.059
DK.23	0.0040	14.9	250	0.067
DK.20	0.0030	8.4	333	0.12
DK.22	0.0030	9.7	333	0.10
DK.17	0.0020	6.3	500	0.16
DK.21	0.0020	6.5	500	0.15
DK.24	0.0015	5.3	667	0.19
DK.27	0.0012	5.0	833	0.20
DK.28	0.0011	4.7	909	0.21
DK.18	0.0010	5.9	1000	0.17
DK.29	0.0010	3.9	1000	0.26

All the above polymerizations were carried out at 50°C. and atmospheric pressure for 3 hours using a 0.5 mMolar concentration of aluminium triethyl and dodecyl magnesium bromide prepared $TiCl_3$.

Table VII

Rate of polymerization versus temperature

Results shown in Figures 22, 23 and 27.

Run No.	Temp. $^{o}C.$	Polyn. rate ($dm^3.hr.^{-1}$)	$TiCl_3$ conc. (millimolar)	Specific polyn. rate, R ($dm^3 hr^{-1} mM^{-1}$)	$Log_{10}R$	10^3
DK.39	0	6.8	0.20	34	1.53	3.66
DK.42	0	4.6	0.29	16	1.21	3.66
DK.40	15	9.8	0.10	98	1.99	3.47
DK.41	15	9.0	0.10	90	1.95	3.47
DK.32	30	9.8	0.02	490 ,	2.69	3.30
DK.33	30	12.5	0.05	250	2.38	3.30
DK.38	40	15.4	0.01	1540	3.19	3.19
DK.2	50	29.3	0.01	2930	3.47	3.10
DK.7	50	30.3	0.01	3030	3.48	3.10
DK.36	60	30.2	0.01	3020	3.48	3.00
DK.37	60	26.8	0.01	2680	3.43	3.00

All the above polymerizations were carried out at amospheric pressure for 3 hours using dodecyl magnesium bromide prepared $TiCl_3$ and a 0.5 mM concentration of aluminium triethyl.

Table VIII

Variation in molecular weight of polymer versus time

Results for Figure 24

Time min.	Limiting viscosity number ($cm^3gm^{-1} \times 10^{-2}$)	Number average molecular weight $\times 10^{-5}$
0	-	-
30	13.61	6.60
60	13.92	6.79
120	16.08	8.09
180	16.37	8.27
240	18.54	9.63
300	18.18	9.40
360	17.79	9.15

These results were obtained for Run No. DK.45 which was carried out at 50°C. and atmospheric pressure. An aluminium triethyl concentration of 0.5 millimolar and a dodecyl magnesium bromide prepared $TiCl_3$ concentration of 0.01 millimolar were used.

Table IX

Effect of the concentration of aluminium triethyl upon the molecular weight of the polymer

Results for Figure 25.

Run No.	Aluminium triethyl concn. (millimolar)	Limiting viscosity number ($cm^3gm^{-1} \times 10^{-2}$)	Number average molecular weight ($\bar{M}_n \times 10^{-5}$)
DK.6	0.06	21.97	11.84
DK.5	0.11	19.99	10.55
DK.12	0.15	18.56	9.63
DK.11	0.22	19.61	10.31
DK.2	0.48	23.08	12.57
DK.7	0.53	18.29	9.47
DK.1	0.96	18.25	9.44
DK.8	1.10	17.17	8.76
DK.9	2.20	13.76	6.69
DK.3	5.05	14.46	7.11
DK.4	8.96	12.46	5.93

All the above experiments were carried out at 50°C. and atmospheric pressure for 3 hours using aluminium triethyl and 0.01 mMolar concentration of dodecyl magnesium bromide prepared $TiCl_3$

Table X

Effect of temperature upon the molecular weight of the polymer

Results shown in Figure 26 and 27.

Run No.	Temp., °C.	Limiting viscosity number ($cm^3 gm^{-1} \times 10^{-2}$)	Number Average molecular weight ($\bar{M}_n \times 10^{-5}$)	$10^3/T$ ($^oK^{-1}$)
DK.42	0	17.75	9.13	3.66
DK.44	0	15.95	8.01	3.66
DK.40	15	17.17	8.76	3.47
DK.43	15	16.90	8.60	3.47
DK.32	30	25.14	13.95	3.30
DK.33	30	24.82	13.74	3.30
DK.38	40	22.42	12.13	3.19
DK.7	50	18.29	9.47	3.10
DK.30	50	21.12	11.29	3.10
DK.31	50	22.62	12.27	3.10
DK.45	50	16.37	8.27	3.10
DK.36	60	14.98	7.42	3.00
DK.37	60	13.36	6.45	3.00

All the above experiments were carried out at atmospheric pressure for 3 hours using a 0.5 millimolar concentration of aluminium triethyl and dodecyl magnesium bromide prepared $TiCl_3$.

Table XI

The variation of the molecular weight of the polymer versus time at different temperatures

Results shown in Figure 28

Time, min.	DK.30, DK.31 at 50°C.*		DK.34 at 30°C.		DK.43 at 15°C.		DK.44 at 0°C.	
	LVN	$\bar{M}_n$	LVN	$\bar{M}_n$	LVN	$\bar{M}_n$	LVN	$\bar{M}_n$
5	7.90	3.40	12.21	5.78	12.98	6.23	12.00	5.66
10	10.89	5.03	17.93	9.24	10.66	4.90	13.50	6.54
15	11.58	5.42	20.66	10.98	-	-	-	-
20	12.95	6.21	19.88	10.48	-	-	-	-
25	13.37	6.46	-	-	-	-	-	-
30	15.76	7.89	20.75	11.04	13.94	6.80	15.03	7.45
40	15.65	7.83	-	-	-	-	-	-
50	15.93	8.00	24.33	13.41	-	-	-	-
60	15.96	8.02	25.43	14.15	16.87	8.58	18.94	9.88
75	16.84	8.56	20.69	11.01	-	-	-	-
90	16.86	8.57	27.56	15.61	-	-	-	-
105	16.47	8.33	27.58	15.62	-	-	-	-
120	19.31	10.11	-	-	22.00	11.86	18.52	9.61
135	20.11	10.63	30.17	17.43	-	-	-	-
150	19.65	10.33	29.29	16.81	-	-	-	-
180	21.82	11.74	29.00	16.61	16.90	8.60	15.95	8.01

* Values averaged from Experiments DK.30 and DK.31.

Units used in the above table are as follows:

$$\text{I.V.N.} = cm^3 gm^{-1}$$

$$\bar{M}_n = \bar{M}_n \times 10^{-5}$$

All the above experiments were carried out at atmospheric pressure using 0.5 millimolar concentration of aluminium

triethyl and dodecyl magnesium bromide prepared $TiCl_3$.

Table XII

The variation of the molecular weight of the polymer versus time for conventional catalyst

Results shown in Figure 29.

Time mins.	Limiting viscosity number ($cm^3 gm^{-1} \times 10^{-2}$)	Number average molecular weight ($\bar{M}_n \times 10^{-5}$)
5	18.74	9.75
10	16.62	8.42
30	21.07	11.25
60	23.91	13.13
105	26.69	15.01
120	22.68	12.31
180	29.82	17.18

This experiment was carried out at 50°C. and atmospheric pressure using 10 millimolar concentration of aluminium diethyl chloride and a 0.35 millimolar concentration of aluminium diethyl chloride prepared γ-$TiCl_3$.

Table XIII

$Y_t/(\bar{M}_n)_t$ versus Y_t for the magnesium reduced catalyst.

Results shown in Figures 30 - 33.

Time mins.	Run No.	DK.7	DK.30/31		DK.32	DK.34	
	Temp. °C	50	50	50	30	30	30
		Y_t(gm)	$\bar{M}_n \times 10^{-5}$	$Y_t/(\bar{M}_n)_t \times 10^5$	Y_t(gm)	$\bar{M}_n \times 10^{-5}$	$Y_t/(\bar{M}_n)_t \times 10^5$
5		3.72	3.40	1.09	1.78	5.78	0.31
10		5.24	5.03	1.04	2.70	9.24	0.29
15		8.47	5.42	1.56	3.63	10.98	0.33
20		11.58	6.21	1.86	4.50	10.48	0.43
25		14.69	6.46	2.27	-	-	-
30		17.79	7.89	2.25	6.13	11.04	0.56
40		24.00	7.83	3.07	-	-	-
50		30.34	8.00	3.79	9.06	13.41	0.68
60		36.44	8.02	4.54	10.48	14.15	0.74
75		45.52	8.56	5.32	12.22	11.01	1.11
90		54.07	8.57	6.31	14.44	15.61	0.93
105		62.34	8.33	7.48	16.49	15.62	1.06
120		70.25	10.11	6.95	-	-	-
135		77.94	10.63	7.33	20.42	17.43	1.17
150		85.41	10.33	8.27	22.15	16.81	1.32
180		99.40	11.74	8.47	23.80	16.61	1.43
	Run No.	DK.40	DK.43		DK.42	DK.44	
	Temp. °C	15	15	15	0	0	0
5		3.16	6.23	0.51	3.04	5.66	0.54
10		5.59	4.90	1.14	5.65	6.54	0.86
30		10.21	6.80	1.50	8.76	7.45	1.18
60		15.16	8.58	1.77	11.13	9.88	1.13
120		21.93	11.86	1.85	14.13	9.61	1.47
180		26.90	8.60	3.13	15.80	8.01	1.97

Conditions of experiments as stated in Appendix - Table XI.

Table XIV

$Y_t/(\bar{M}_n)_t$ versus Y_t for the conventional catalyst

Results shown in Figure 34.

Time mins.	Y_t gm.	$(\bar{M}_n)_t$ $\bar{M}_n \times 10^{-5}$	$Y_t/(\bar{M}_n)_t$ $\times 10^5$
5	1.23	9.75	0.13
10	3.49	8.42	0.41
30	12.17	11.25	1.08
60	26.74	13.13	2.04
105	49.87	15.01	3.32
120	57.48	12.31	4.67
180	91.03	17.18	5.30

Experiments carried out at 50°C.. Conditions as stated in Appendix - Table XII. Y_t results from Run No. AK.47, and $(\bar{M}_n)_t$ results from Run No. AK.50.

Table XV

Parameters used in the g.p.c. analysis

See Table 8

G.P.C. Operating Variables

Columns:

4 columns.

i) 70 - 200 nm.

ii) $1.5 \times 10^3 - 5 \times 10^3$ n.m.

iii) $1.5 \times 10^4 - 7.5 \times 10^4$ n.m.

iv) $5 \times 10^5 - 10^6$ n.m.

Flow rate:

1 cm^3 per minute.

Solvent:

o-dichlorobenzene + 0.1% Ionox 330 as antioxidant.

Temperature:

137 - 138°C.

Calibration:

Polystyrene.

Interpretation:

Calibration conversion to polyethylene is made using the following Mark-Houwink parameters.

Mark-Houwink constants

$$[\eta] = KM^{\alpha}$$

Polystyrene: $K = 1.38 \times 10^{-4}$

$\alpha = 0.70$

Polyethylene: $K = 5.06 \times 10^{-4}$

$\alpha = 0.70$